OPTICAL STUDIES
ON THE GROWTH OF SUCROSE
CRYSTALS IN SOLUTION.

(PRELIMINARY STUDIES).

by

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A C K N O W L E D G M E N T S.

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C O N T E N T S.

C O N T E N T S. (continued)

ABSTRACT

The growth of sucrose crystals from aqueous solution has been investigated.

A Review of the previous work on the growth of crystals from solution has been made.

A new interference technique has been applied to the problem in the employment of the Mach-Zehnder interferometer. This has the advantage over any other type of interferometer for two reasons. One is that the fringes can be localized in any desired plane. (In the present case this was the plane of the growing crystal). The second is that in an interferometer such as the Michelson type the light beam traverses the object in two directions i.e. in going from the beam splitter and returning to it. If the object has considerable local variations in refractive index there can be some displacement of the beam, which on its return journey does not pass exactly along the same path that it did initially. This might lead to fringe confusion. In the Mach-Zehnder system the beam passes through the object in one direction only and this difficulty does not arise.

The changes in refractive index of the solution were measured for a number of crystals growing from solution and hence the concentration along a face was determined. This was in many cases a maximum at the corners of the crystal but faces were

observed which had a uniform concentration along their length for quite a long period of time. The value in all cases was greater than solubility concentration.

The effect of convection on growth was investigated. When a crystal grows a stream of depleted solution can be seen rising from the crystal. This was observed to become established at a corner of the crystal. The concentration of the solution at the centre of this stream has been measured and was approximately 1% less than that in the bulk of the solution. The streaming effect would also appear to affect the rate of growth, which increases when the effect is established and fluctuates when the streaming undergoes variations.

CHAPTER I.

THEORIES OF CRYSTAL GROWTH

1. (i). Introduction

A brief outline of the main theories of crystal growth will be given; the classical theories which may be considered under the heading of the theory of ideal perfect growth and the more recent theory of dislocations on ideal imperfect growth. In spite of the many successes of crystal growth in recent years there is still a lack of a theory of growth of real crystals, and there seems a large divergence between theoretical and practical work on the subject.

1. (ii). Theories involving Surface Energy

The first theory put forward which received serious attention in the field of crystal growth was that due to Curie[1] (1885). This was based on the theoretical work of Gibbs[2] (1878) who provided a clear definition of surface free energy, by which the concept of Surface Tension is made applicable in solids as well as liquids. Curie proposed an intimate connection between crystalline form and surface energy. The work done in extending the crystal surface would be at the expense of Surface Energy (each possible surface having a different value) and the crystal would strive towards an

equilibrium shape which would be a polygon such that the sum of the products of Surface Energy and area for each side would be a minimum. A necessary consequence of this demanded that simultaneous growth and dissolution could occur at the same time in the growing crystal and this had never been observed.

Wulff [3] extended the theory introducing the concept of different velocities of growth for different faces of a crystal. Supposing that the crystal were constructed with face normals (to a given point in the centre of the crystal) proportional to the measured velocities of growth, this would be a body having minimum Surface Energy.

Marc and Ritzel [4] tried to account for the prediction of simultaneous growth and dissolution but Berthoud [5] gives a critical discussion of the whole problem. He refutes the idea on the grounds that the process is not accompanied by the necessary diminution in Free Energy required by Thermodynamics and is impossible.

1. (iii) Diffusion Theories of Growth

These theories may be regarded as contemporary with the Curie theory but were developed independently of it. Here it was assumed that the process by which matter was exchanged between a crystal and its surrounding solution took place with a reaction velocity very much greater than that for which diffusion could present matter to

or withdraw matter from the crystal surface. Under this assumption the rate of growth would be dependent entirely on diffusion. The concentration at the surface of the crystal would be almost exactly saturation and the solute would travel down a concentration gradient existing in the diffusion zone surrounding the crystal.

If the homogeneous concentration c of a stirred solution containing crystals of total surface area A, is measured from time to time during growth or dissolution it can be deduced that the rate of change dc/dt would be given by the following equation

$$\frac{dc}{dt} = K A (c - c_s) \qquad (1.1)$$

Where c_s is the concentration at the surface of the crystal and is saturation concentration. Noyes and Whitney[6] claimed to have confirmed equation (1.1) for dissolution and it was thought that growth was merely the reverse process. In experiments it was proved that in general there was no reciprocity. Nernst[7] modified the equation introducing δ the thickness of the layer through which diffusion is taking place, deducing the relation

$$\frac{dc}{dt} = \frac{DA}{\delta} (c - c_s)$$

Many workers carried out experiments in an endeavour to confirm the Nernst equation but results pointed to the fact that it was an oversimplification. The original sub microscopic nucleus should

if the Nernst assumption be true always lead to a spherical crystal when grown from solution; whereas it is an observed fact that crystals preserve their typical shape under a wide variety of external conditions.

Some of the results of Marc[8] are worth mentioning in the light of later events. He made a series of experiments with the object of confirming the Nernst equation for growth. Suspecting that impurities might be having an effect, he introduced foreign substances into solution and obtained marked effects with organic dyestuffs. The effect was always to retard growth and in certain instances to stop it altogether. It was notable that just those dyes which coloured (adsorbed onto) readily the crystals were those which had a retarding effect on growth. The fact that they had no effect on dissolution indicated that their action was not that of isolating the crystal from the solution. It was likely therefore that the process of growth was connected with adsorption onto the crystal surface and Marc postulated that solute molecules entered an adsorbed layer in which they were brought into a fit state (say of orientation) for incorporation into the crystals. If foreign molecules were present which adsorbed onto the crystal surface but did not incorporate into it, they would hinder the process taking place in the adsorbed layer and so retard growth.

The Nernst equation suffered from the disadvantage that it

predicted that all faces of all crystals would grow at the same rate under similar external conditions. This was due to the assumption that the reaction rate for the incorporation of material into the crystal, at its surface, is extremely high compared with the rate of arrival of fresh matter by diffusion.

The next development to be reviewed will be the modification of the Nernst equation to include an operative factor characteristic of the crystal and independent of diffusion. Berthoud[5] proposed that the concentration at the crystal surface is not, as assumed by Nernst, saturation concentration, but during growth has some value higher than this c'.

The saturation in the bulk of the solution c is the same as before and so is saturation concentration c_s. The concentration c' however can be different for different faces of the crystal and this will depend on a specific factor called the coefficient of crystallisation velocity k. If growth is rapid k would have a large value and the value of c' would fall if fresh matter could not be supplied at a fast enough rate by diffusion. The value of c' however would always be greater than c_s and when a steady state has been achieved the crystal grows at a rate proportional to the magnitude of this supersaturation. In the simplest case k may be taken as proportional to the velocity of growth which is again proportional to the supersaturation $(c' - c_s)$.

Using the Nernst assumption that the diffusion zone has been reduced to a small thickness δ, the steady state condition resulting from the two independent processes of diffusion and crystallisation is represented as follows -

$$\frac{dc}{dt} = \frac{DA}{\delta} (c - c')$$

This equation representing the operation of diffusion down the concentration gradient $(c - c')$ and

$$\frac{dc}{dt} = k A (c' - c_s)$$

representing the reaction at the crystal surface.

The two equations in combination yield

$$\frac{dc}{dt} = \frac{DA}{\delta + D/k} (c - c_s) \qquad (1.2)$$

$$c' = \frac{c_s + \delta D/k \; c}{1 + \delta D/k} \qquad (1.3)$$

Using the Nernst assumption k is infinite compared with D and the fraction D/k vanishes so that equation (1.2) reverts to the original equation (1.1) and equation (1.3) becomes $c' = c_s$ i.e. the concentration at the surface is saturation which was a consequence of the Nernst assumption.

From the practical point of view the equations suffer from the disadvantage that the residual diffusion zone δ is an indeterminate quantity, and that the diffusion coefficient D is somewhat unusually defined.

An advance on Berthoud's treatment is afforded by Valeton[9]. In this theory the same basic assumption is made namely that rate of growth is proportional to supersaturation at the crystal surface in the steady state. The difficulty of an unknown thickness of diffusion zone is avoided by considering a crystal growing in stagnant, unstirred conditions immersed in a supersaturated solution in a vessel very large compared with the dimensions of the crystal.

In addition mathematical difficulties inherent in solving the diffusion problem for a polygonal crystal are avoided by considering the crystal as a sphere. The broad predictions of the equations obtained are considered similar to those from a rigorous treatment with a polygonal crystal.

In a steady state the equations obtained are

$$G = \frac{D\,(c_o - c_s)}{D/k + a} \qquad (1.4.)$$

$$C_a = \frac{D/k\ c_o + a\ c_s}{D/k + a} \qquad (1.5.)$$

where C_a is the concentration at the surface of the crystal radius a, G is the mass per second per unit area incorporated into the crystal, c_o is the concentration in the bulk of the solution and D is the diffusion constant here more rigorously defined as in Fick's Law.

If k is large compared with D equation (5) reduces to $C_a = C_s$ and is again in accordance with the historical Nernst

assumption in which the facial rate of advance is dependent only on diffusion geometry.

1. (iv) Adsorption Layer theories

As mentioned above Marc proposed the existence of a layer of increased concentration surrounding the outermost lattice planes of the crystal. He specifically called it an absorbed layer but did not estimate its thickness, suggesting that it should at the most be no more than a few molecules deep. The same difficulty lies in the way of the layer necessitated by the diffusion theories and the experimental work of Miers, which pointed to a layer of increased concentration at the surface of the crystal without yielding anything specific with regard to the depth of the layer. The first of the growth theories introducing the idea of a true adsorption layer is that due to Volmer [10] and his co-workers. They were studying the growth of mercury crystals from the vapour and claimed that the very thin plates produced could not be accounted for if molecules were assumed to be incorporated into the face of the crystal where they first struck.

According to the theory a crystallising particle only loses a portion of its latent heat on arrival at the crystal surface. Through this loss it is effectively bound to the surface but has lateral mobility. All other particles in the neighbourhood are in a condition similar to this. Together they constitute an adsorbed

layer which interposes itself between the crystal surface and the surrounding solution.

A particle in this state can (a) evaporate again (b) migrate to another face (c) coagulate with other molecules to form a two dimensional nucleus. These nuclei would eventually take up positions of rest and originate new planes and so the crystal would grow. Volmer regards the velocity of spread of the crystallised portion of the layer as approximately proportional to the square of the density of particles within it.

The Volmer theory was the first to introduce the idea of a state of binding intermediate between the vapour phase and the true solid phase. This "adsorbed" stage was proposed as a necessary state in which molecules found the correct energy conditions for incorporation into the crystal lattice.

Brandes[11] worked on lines similar to Volmer. He too assumed that growth was discontinuous (plane by plane) and outlined a theory wherein the different rates of growth of faces are ascribed to different chances of formation of two dimensional crystal nuclei in the outer adsorbed layer. The nuclei are supposed capable of forming anywhere on the surface. Their frequency of formation is made to depend on the chance of their achieving a size such that the tendency for them to redissolve under influence of their boundary energy is overcome. Brande's theory is incomplete in that it

ignores any connection between the formation of a nucleus and the position on the underlying surface where it is formed. There is experimental evidence that certain points on the surface are more likely to originate new planes than others. A satisfactory theory must take this into account.

1. (v) Theories involving the Fine Structure of the Crystal Surface

The above theories neglected to take into account that there might be amongst the various positions on a growing surface, differences in the case of formation of an elementary two dimensional nucleus. It is in this direction that a large part of the theoretical speculation is turned from now on. In Brande's theory the two dimensional nucleus possessed a fluid "boundary energy" and its formation could be thermo-dynamically handled. In these later theories the technique is to imagine the plane built molecule by molecule. It is possible from structural data to calculate the force fields around a crystal surface when a single crystallizing particle approaches a surface and thus to infer the probability of deposition. The binding energy is calculated for each possible location of a new molecule. Those locations with the greatest binding energy will be most stable; that is the molecules in them will be likely to stay long enough to be joined by others. In locations of least binding energy molecules are liable to be thermally ejected before being joined by others. A completely new plane will

be started at a position of greatest binding energy or at one or more of such positions if there are several not differing greatly in binding energy. Thereafter it will develop by stages in order of binding energy. If the possible stages differ markedly in binding energy the chances are that the subsequent order of events will be indeterminate. It will be seen that this outlook leads to a kinetic rather than thermodynamical treatment.

Stranski[12] inaugurated this method for the NaCl cube. The force on an ion in the lattice falls off so rapidly with distance that he considered the effect of nearest neighbours only when calculating the work of separation (defined as the work needed to remove an ion from the position considered to infinity) for various positions. Stranski provided a table of values for all the chief positions ranging from corners, edges and centre of a complete plane to the various positions on partially completed planes. He did this for the three chief cubic planes. Taking first the (100) face cube, the conclusion was that in conditions not too far removed from saturation planes would start from the edges or corners of the cube, but not from the centre of the cube faces. The subsequent spread of a new plane would be row-by-row because the position at the end of a partially completed row out-values all others in the work of separation. When a row was complete a new one would much more likely be started on the partially completed plane, than that another partial

plane would be started at a corner.

The separation work of the position at the end of the partial row, which has been called the "repeatable" stage, would determine the saturation concentration of the face. If the outside conditions were supersaturated with regard to this stage, the plane would complete itself, for after each row is completed it needs only a chance fluctuation in local concentration to start a new row, which then fills up spontaneously. If the environment were undersaturated with regard to the repeatable stage, the rows would strip down and remain stripped until the necessary chance fluctuation broke down the complete plane and started the spontaneous process again.

Equilibrium between the surface and environment would therefore mean equilibrium between the repeatable stage and environment.

As regards (110) faces, the tendency would be to transform what might have started as a perfect (110) face into one comprising echelons of (100) type. (111) faces were found to have a negative work of separation for one of the positions and so cannot exist unless the position of negative work of separation is "sealed off" by selective absorption of some foreign molecule. It is in fact one of the advantages of this type of theory that it allows selective absorption to alter the order of events and so make a start in explaining the observed changes of habit brought about by specific impurities.

Another author, Kossel[13], argued on almost identical lines to

Stranski. The rate of growth of an ionic cube is determined by the most difficult step, that of starting a new plane. Small quantities of impurity, if it adsorbs selectively onto corners and edges can prevent growth if the supersaturation is insufficient to bring about the most difficult step of all, that of nucleus formation on to the middle of the complete face.

Because of the importance of corners and edges the type of neighbouring face, if other than cubic, can effect the rate of growth.

The situation for non ionic crystals is different; new planes should best start from the centre of a face. But the binding of edges and corners is weak relatively, and at equilibrium they would be expected to be unoccupied on the average giving rise to (110) and (111) faces respectively. If the environment is then allowed to become supersaturated these blunted edges and corners would fill up first, and afterwards the new plane would start from the middle of the complete plane. Stranski[14].

The Kossel-Stranski method of interpretation of crystal growth and habit leads in later papers to detailed attempts to explain the external form of simple types of crystal. These developments will not be reviewed here; it will be sufficient to retain the principle of nucleation points and growth by the spreading of layers.

Observations carried out by Bunn and Emmett[15] on a wide range of ionic crystals show that layers very often start, not from the

edges or corners of the crystal face but from the centre, spreading outwards towards the edges.

This would appear to show that in fact, beyond accepting the principle of the Kossel-Stanski theory one is not justified in view of the actual complexity of conditions in employing their theory to predict the actual positions of growing points. In spite of the great simplifications the theory was a great step forward relative to the previous purely thermodynamical ones. The theory gives a detailed explanation of the multifacial shapes of crystals, of the discontinuous character of growth and the important concepts of edge growth sites and rèpetition in growth derived from it.

The theory implies that a range of supersaturation exists within which a crystal bounded by smooth faces will not grow.

1. (vi). Theory of Growth of ideal imperfect crystals.

According to the above theory, when all surfaces of high index have disappeared the crystal will continue to grow by two dimensional nucleation on surfaces of low index. As in all nucleation processes the probability of formation of these two dimensional nuclei is a very sensitive function of supersaturation. This probability is quite negligible below a certain critical supersaturation and increases very rapidly above it. Assuming reasonable values for the edge energy of the two dimensional nucleus it is recognized that this critical supersaturation should be of the order of 50%.

Experimentally the critical supersaturation for growth has been observed to be very much lower than this; 0.8% was the value found by Volmer and Schultze[16] for the growth of iodine crystals from vapour. In fact the most well developed crystals are formed at low supersaturations.

Burton, Cabrera and Frank[17] showed that the probability of formation of nuclei at the supersaturations at which real crystals grow would be according to the above theories absolutely negligible. They concluded that the growth of crystals under low supersaturations could only be explained by recognizing that crystals which grow are not perfect, and that their imperfections will provide the steps required for growth, making two dimensional nucleation unnecessary. In particular they considered the screw dislocation which was first introduced by Burgers[18] (1939) and emerging on the face of a crystal provides it with a step. This step is self perpetuating in the sense that when one, two or any number of layers of atoms have been laid down on the surface the step remains.

The process of growth under these circumstances will be similar to that outlined in the case of a perfect crystal with a step. The step provided by the screw dislocation will have kinks as before and when atoms are adsorbed on the surface they diffuse to the step and finally to the kinks where they are adsorbed for the building up of a crystal; and thus the step advances. In the case of a perfect

crystal the step extended all the way across the crystal surface so that it could advance parallel to itself thereby completing a new layer.

The step provided by the emergence of a screw dislocation however terminates at the dislocation point, where it remains fixed. Hence when growth takes place, the step can advance only by rotating round the dislocation point somewhat like the hand of a clock. When a steady state has been reached the whole spiral will rotate uniformly about the dislocation. Griffin[19] (1950) published the first experimental observation in support of the theory of growth of crystals by spiral mechanism. Using bright field microscopy he observed markings on beryl crystals. Calibration by multiple beam interference fringes showed that the step height was less than 34.Å i.e. less than four unit cells of the crystal. The volume of experimental observations in support of the spiral mechanism theory of crystal growth has since grown considerably.

This concludes the general review of the main theories of crystal growth. More complete accounts have been given by Wells[20] and Buckley[21]. A discussion of various aspects of the theories can be found in the Disc. Faraday. Soc. 5 (1949) and Growth and Perfection of Crystals (Wiley 1958).

Despite all these theories there still seems to be a lack of theory of fundamental processes and one is left with the choice of

a wide number of explanations to interpret provisionally any new experimental results.

CHAPTER II

PREVIOUS WORK ON THE GROWTH OF CRYSTALS FROM SOLUTION.

An account will now be given of previous experiments carried out on the growth of crystals from solution and how they form a basis for the present work.

When a crystal grows from a supersaturated solution the concentration of the solution contiguous to the crystal is depleted a concentration gradient results and fresh solute arrives by diffusion down this gradient. This process may be divided into two parts - the "taking" of solute by the crystal from the solution i.e. the reaction at the surface and the diffusion process by which the solution in contact with the crystal is replenished. A knowledge of the supersaturation at the surface is necessary for it may control the rate at which fresh material is incorporated into the crystal and also the concentration gradient established depends on the supersaturation at the face as well as the initial supersaturation of the solution.

It was at one time supposed that the concentration at the surface sinks to the solubility value; in 1903 Miers [22] by measuring the angle of total internal reflection at a growing crystal face determined the refractive index of the solution and hence its composition and established that the solution at the face is

appreciably supersaturated; he found this so for three substances alum, sodium chlorate, sodium nitrate. In the later theoretical speculations such as those of Berthoud and Valeton the prevalent idea was that the rate of growth of a given type of face is some function of the supersaturation existing there, the underlying conception being that the supersaturation is a measure of the driving force for deposition. (Crystals of different types being characterised by different rates of growth at the same supersaturation). The conception seemed reasonable, Bunn[23] and Berg[24] measured simultaneously the rates of growth of crystal faces, the supersaturation at the face and the concentration gradients around the crystal.

They grew single crystals of sodium chlorate in a thin film of aqueous solution between horizontally mounted optically plane glass plates. In this way the crystal was limited, growth was constrained to the four faces in the plane of the film and was considered to be reduced practically to a two-dimensional process. In addition as it was a microscopic process convection was considered as negligible. The glass plates were half silvered, together forming a wedge and under the microscope using parallel monochromatic transmitted light a system of interference fringes was obtained. The distortion of these fringes was a measure of changes in refractive index and hence concentration. Photographs were taken at intervals

and subsequently measured in detail. Sodium chlorate was chosen, as it is cubic, and strongly supersaturated solutions can be prepared in which unwanted crystal nuclei are less readily formed than for other substances. Further experimental details can be found in the paper by Berg[24].

The results obtained from these experiments were unexpectedly complex. It was found that -

(i) the concentration was not uniform along a face but was lowest at its centre rising on each side to the corners.

(ii) the component of the concentration gradient normal to the face which is proportional to the exit of solute per unit area from solution was also not uniform. It was highest at the centres and fell towards the corners.

(iii) faces of one crystal, though all of the same type and initially in contact with solution of the same concentration usually grew at different rates and sometimes stopped growing altogether.

(iv) there was a tendency for the slower growing faces of one crystal to be in contact with solution of higher concentration.

Bunn concluded from these results that there was no correlation between the rate of growth of a particular type of face and the supersaturation at the face; that a growing crystal surface is not uniform as assumed in all the theories and surface forces must vary at different points along its length and hence the variation in

concentration of the solution.

He considered his other results in relation to the phenomenon of layer formation. The theories of Kossel, Stranski, Brandes and Volmer previously mentioned all support the idea, at any rate for ionic crystals of the NaCl type of structure, that material is deposited on the faces in successive layers but direct experimental evidence on the matter on the ionic or monomolecular is not available. The first definite indication of growth by layer deposition was reported by Marcelin [25] (1918). He studied the growth of m - toluidine crystals, which grows in extremely thin plates from alcoholic solutions. These plates were sufficiently thin to exhibit Newton's colours so that growth in depth and surface area could be observed simultaneously. It was calculated that in some circumstances the layers thus revealed were only a few tens of Angstrom - in fact only a few molecules thick. Volmer [10] observed similar thin layers on crystals of PbI_2. Kowarski [26] extended the work to growth of p - toluidine from vapour. He found that layers were usually initiated from the edges of faces and particularly at the point of intersection of the edge with a neighbouring crystal. Bunn and Emmett [15] made an extensive survey of growth layers on crystals of many different substances. The layers observed varied in thickness from several hundred to a few thousand Angstrom.

One of their most surprising results was the observation that

generally layers originated at the face centres and not at the corners and edges as theoretically predicted. These results may be considered as a result of conditions on the surface of the crystal or alternatively as due to conditions in the solution.

Bunn combined these observations with the information on the concentration gradients existing round the crystal. As the supersaturation was lowest at the face centres the conclusion was that this could not be the cause of layers originating there. The other condition which varied was the concentration gradient normal to the face which controls the diffusive flow of solute. As stated above this was observed to be a maximum at the face centre. This arrival of excess solute at the face centre could not be due to surface conditions and therefore Bunn turned to the consideration of the diffusion field around the growing crystal.

Berg had concluded that if more solute arrives at the face centres than at the edges, and the face remains flat, the excess must be dissipated by surface migration. This would be in the form of a Volmer adsorbed layer.

Accepting this fact Bunn stated that the process of radial inward diffusion to a polyhedral crystal can explain the result. If there was no surface migration the crystal would "take" from the solution uniform amounts of solute all along the face, and this would require the diffusion field to set up concentration gradients

to make this possible. If surface migration takes place however the diffusion field is not restricted to delivering uniform amounts of solute along the face, since any non uniformity can be dissipated by this surface migration. Under these conditions the radial inward diffusion process would tend to deliver less solute to the corners than the face centres.

This conclusion not only suggests the cause for the origination of layers at the face centres but also has implications on changes in rate of growth; for if the normal inception of layers at face centres is due to diffusive convergence of excess solute there when the diffusion field is undisturbed, then any effects on the diffusion field due to convection currents would be likely to change the rate of inception unequally on different faces.

The other results of the experiment were considered by Bunn to be due to the fact that the growth of the crystal is possible due to the maintenance of high index surfaces.

The fact that crystals do grow at moderate supersaturations can be explained either by Frank's dislocation theory or by assuming that growing surfaces are not of low index. Bunn's observations on layer growth seemed to point to the fact that deposition from solution takes place on the edge of spreading layers which on the scale observable in the optical microscope are of high index. If this is the case, then if there is a tendency for the surfaces to

"heal" i.e. become a surface of low index the growth rate would slow down, and if they healed completely growth would be severely inhibited; it is possible that this could explain the fact why some faces stop growing altogether although in contact with solution of high supersaturation.

A question which would arise out of this is why do not solute molecules deposit in such a way that low index surfaces are formed immediately? Bunn states that it may be that if solute molecules are supplied at a fast rate by the diffusion field then deposition occurs in an indiscriminate way such that high index surfaces are maintained.

Humphreys - Owen[27] (1949) repeated and extended these experiments using the same technique. He confirmed certain results and proved that the crystal grew approximately as predicted by Nernst and others; that is on the assumption that the reaction velocity of the crystallisation process is high compared with that of diffusion, resulting in a law of growth dependent only on diffusion.

This conclusion was only approximate and Humphreys-Owen stated that there were two processes which modified the action. Firstly a mechanism at the surface which led to a variation in concentration and inflow per unit area along the face; this is accounted for by the existence of the adsorbed layer as postulated by Berg. Secondly there was a tendency for the face to be inhibited to varying degrees

for given external diffusive conditions.

The fact that a crystal does not incorporate new material into its surface at any position of the face implies inhibition of a certain degree. Humphreys-Owen defined inhibition as used above as something which occurs over and above this normal effect. For uninhibited growth the steady state concentration at the surface was found to be saturation i.e. solubility concentration within the limits of accuracy of the experiments. The rise in value of concentration towards corners was a function of the main diffusion head. In the case of inhibited growth the steady state concentration at the face centre is found to have a higher value but the concentration at the corners is not affected. This higher concentration at the boundary surface with solution is "saturated" - this follows from the fact that it is constant with time - but this "saturation" value is not that which in the theories constructed,has normally been supposed to represent the equilibrium between the solution and the naked crystal. This latter is the concentration at which the crystal neither grows nor dissolves. If the surrounding solution is not directly in contact with the crystal face but with an adsorbed Volmer layer between the crystal and solution these results can be explained.

Assuming that the growth process can give rise to variations in the density of this layer, the concentration and its gradients

would be a direct function of this density, and could vary along a face and from face to face. For any value of layer density there would exist an equilibrium value of concentration outside it. The higher the layer density the higher the concentration of outside solution in equilibrium with it and vice versa. Also the higher the layer density, the lower the intake from the external solution, since the layer would be more nearly saturated. Crystal growth would tend to denude the layer, and so any inhibitions of growth would raise the steady state density of the layer and hence the concentration of the solution outside of it. Generally speaking fast growth would be associated with low layer density, high gradient and low concentration outside. Slow growth would be accompanied in general by high layer density, low gradient into the layer and high concentration. From this point of view the postulate of the Volmer layer, of variable density, in equilibrium with the crystal surface and surrounding solution is plausible. This is an explanation of the effect reduced to the simplest terms i.e. consideration of an isolated face. It must be remembered that the growth of the crystal takes place in a single diffusion field and neighbouring faces do tend to modify results.

Humphreys-Owen could offer no cause for the partial or total inhibition of faces. The effect appeared to some extent to be general but no crystal was observed will all four faces behaving

similarly. The effect was discontinuous but persisted in some cases for long periods. Complete stoppage of growth in some cases was thought to indicate 'poisoning' of the corners of the crystal, since Humphreys-Owen found it difficult to imagine how poisoning of the whole face could occur in the absence of deliberately introduced impurities. In support of this conclusion is the observation that in a high supersaturation a stopped face restarted growth by nucleation on the main part of the face, suggesting that nucleation at the corners was the normal process as theoretically calculated, but had been prevented for some reason.

As regards the information gained on the nature of the adsorbed layer, the experimental result of the variation of the normal gradient of concentration was taken as conclusive proof that flow along the face of the crystal existed. Humphreys-Owen calculated that if this layer is taken to be mono-molecular and transport is taken to occur in a layer of molecular height 10^{-8} cms., it corresponds to a flow per sec. per unit area of the order of 1 gm/sec/sq.cm. Even if the height of the layer was underestimated these results pointed to a greatly increased diffusion constant of the layer compared to that of the solution.

Humphreys-Owen also comments on the simple adsorbed layer theory as postulated by Berg. This hypothesis ignores the solvent and assumes the layer contains only solute. The experimental fact

is that concentration is high and intake low at the corners and at the centre the reverse is true. To account for the fact that the crystal face grows as a plane there must be flow in the layer from the centre to the corners to make up for the deficiency of inflow at the corners. This flow in the layer however would be against the gradient of density. This conclusion as it stands would be unacceptable. Humphreys-Owen considered that the presence of solvent molecules must be taken into account and any theory which ignored the solvent would be unsatisfactory because there is a bulk of experimental evidence pointing to the strongly specific effect of solvent both on pure rate of growth and on crystallographic habit.

If the layer is regarded as a solution of solute in solvent, it might still be possible to have a high density of the layer at the corners and low density at the centre and at the same time a low concentration of solute in the layer at the corners and high concentration at the centre. The former fact would explain the Berg effect and the latter would provide a diffusive flow of solute in the layer in the correct direction to compensate for deficient inflow at the corners.

Humphreys-Owen did observe effects which pointed to layer flow by diffusion from adjacent faces during crystal growth and this effect was superposed on layer flow in the face.

Frank[30] has interpreted several of the above results which can be accounted for by the dislocation theory. Bunn had suggested that the central problem of crystal growth was a study of the factors which would maintain high index surfaces during growth, these however would tend to grow out. The essential importance of dislocations is that they would prevent this happening enabling uncompleted layers on high index surfaces to persist. The fact of growth resistance either at the crystal corner or along a face as observed by Humphreys-Owen is then explained by the fact that these dislocations are very close together or that they are absent. Also changes in rate of growth could arise from a sudden rearrangement of dislocations (since the ability of dislocations to move under very small stresses is one of their fundamental properties). They can also be produced by adsorption of a very small amount of impurity on a step line connecting a dominant pair of dislocations.

Frank also cast doubt on the evidence regarding the existence of an adsorbed layer, which was that there was an excess flux in the middle of each face. This was found to be the case in the experiments carried out by Bunn, Berg and Humphreys-Owen. If there is no special surface migration a crystal preserving its form must have uniform deposition over the surface.

Frank pointed out that the chief source of error in their experiments, which might lead to wrong results, was probably due to

convection. The presence of which would invalidate the assumption that the flux of solute is simply proportional to the concentration gradient.

In this work a completely different interference technique has been employed to study the conditions in the solution round a growing sucrose crystal. The effect of convection on the growth of these crystals has been investigated.

CHAPTER III

THE MACH - ZEHNDER INTERFEROMETER

3. (i). Introduction

In the previous work the mechanism of growth was studied for crystals in solution by using multiple beam fringes in a wedge formed between horizontally mounted optical plates. This was on a microscopic scale, convection was therefore considered to be eliminated and diffusion was thought to be the controlling factor in the process.

In the present work the effect of convection on the growth of sucrose crystals from solution has been investigated. The crystals were mounted in cells supported in a vertical position, and to produce the interference fringes a type of Mach-Zehnder [31, 32, 33] interferometer was used. This is an instrument producing two beam fringes and although the number of degrees of freedom in the movement of the plates makes adjustment difficult, it has the advantage over any other type of interferometer in that is possible to localise the fringes in any desired plane. This is necessary in order that the interference pattern in the solution and the crystal may be simultaneously in focus. The fact that due to the design of the instrument each light ray travels only once through the medium under investigation is also a distinct advantage when

for instance it is compared with the Michelson interferometer. In the latter case to produce fringes it is necessary that each light ray must retrace its original path through the test section. If conditions in the test section cause a divergence from this initial path then the light ray will traverse a different path under different conditions on its return. The resultant interference pattern would be due to the integrated effect of the two paths taken and precise analysis of the fringes could not be made.

3. (ii) Theory of the Instrument

The instrument consists of four optically flat plates P_1 P_2 P_3 P_4. Two of these P_2 and P_3 are coated with a fully reflecting film on one side the two remaining being semi-transparent (Fig.3.1.) These are placed at the corners of a rectangle at an inclination of 45° to the sides. A light beam incident on P_1 is split into two beams of equal intensity, one of which is totally reflected at P_2 along to P_4 where it combines with the other beam which has been totally reflected from P_3. As both beams are coherent interference fringes may be formed.

In the following analysis it is assumed that the plates are supplanted by infinitely thin semitransparent surfaces. (Finite thickness of plates only results in parallel displacement of the central ray and does not affect these results). If the instrument is perfectly adjusted so that the plates are exactly parallel and

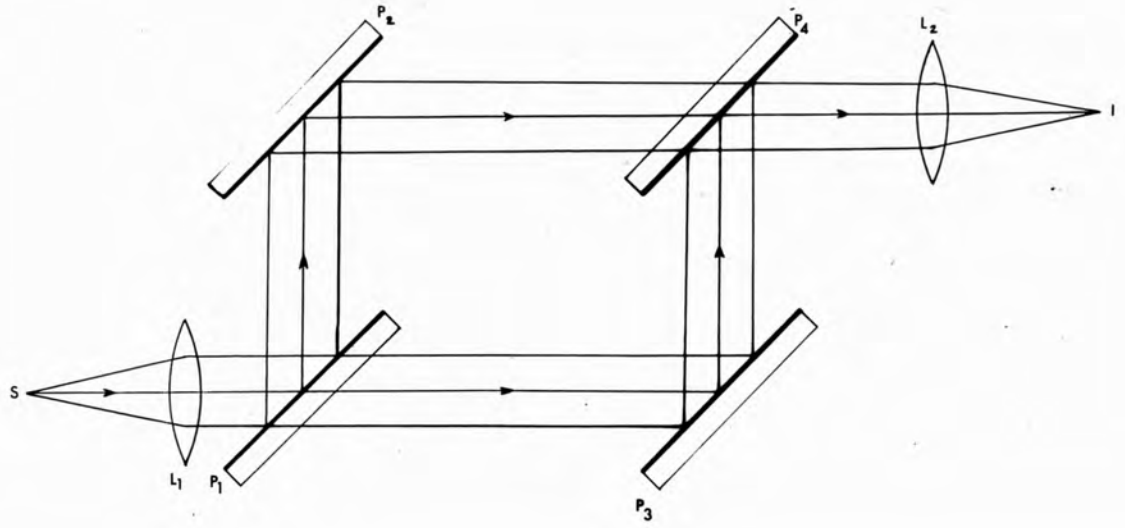

Fig. 3.1. Diagrammatic representation of the Mach - Zehnder interferometer.

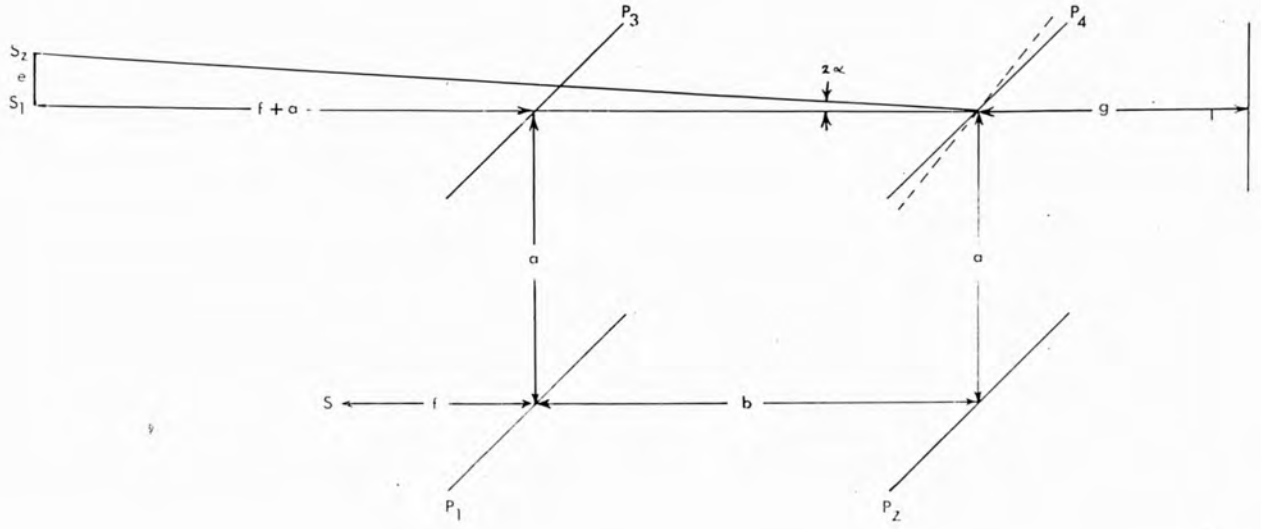

Fig. 3.2. Diagram showing rotation of P_4 through an angle .

at 45° to the sides of the rectangle then both the path lengths, of the divided incident beam, through the instrument are equal and the image S_1 , of a point source S, formed by the rays in the two arms will coincide. If for example P_4 is then rotated through a small angle α about a horizontal axis (perpendicular to the plane of paper in Fig.3.2.) then there are two coherent images S_1 and S_2 produced. The light proceeding from these images is able to produce interference fringes in almost the same way as those obtained in Young's experiment, and the fringes are found to be sharp at any position of the screen P. If the images lie on a horizontal line the fringes will be vertical and vice versa. The distances of these fringes from each other is given, by comparison with Young's experiment, in the following formula.

$$b = \frac{\lambda\,(a + b + f + g)}{e}$$

λ = wavelength of light.

f = distance of source from plate P_1

g = distance of screen from plate P_4

c = distance $S_1\ S_2$

e is given by the angular displacement of P_4 as $e = 2\alpha(f + a + b)$

Thus we have

$$b = \frac{\lambda(f + a + b + g)}{2\alpha(f + a + b)}$$

Narrower fringes are produced by displacing the coherent images

farther from one another by rotation of one of the plates.

With carefully collimated light from a point source sharp fringes are obtained in all planes. In practice only an extended source can be used, fringes may still be observed but they will be sharp in one particular plane only. The reason for this has been shown by Schardin [34]. It must be considered that instead of two coherent point images in the focal plane of lens L_2 we now have many pairs of coherent points covering the whole extent of the images S at I. It is requisite that the planes of symmetry of every coherent pair should intersect on the same line, this line lying in the plane where the fringes appear sharp, and being parallel to the fringes themselves. This line is in fact the central white light fringe of zero order path difference. The effects of a white light source however complicate the analysis of the interferometer considerably and as it is not required for the present work no further account will be given.

For a horizontal linear extended source as treated by Schardin and beginning with all the plates parallel to one another, two plates must in general be rotated about a vertical axis to produce vertical fringes and locate them in a given plane. (For a point source fringes will appear everywhere if only one plate is rotated). A source extending in all directions is to be considered as built up as a series of horizontal linear sources.

In the theory of the formation of interference fringes for an extended source an approximate solution may be obtained by assuming in the simplest case that it consists of two luminous points, S and M. Then an angular displacement of plate P_4 leads to two coherent pairs of point images S_1 S_2 and M_1 M_2. The interference fringes due to these will be superposed where the perpendicular bisectors of S_1 S_2 and M_1 M_2 intersect. In the assumed case this point lies on plate P_4. (since S_1 S_2 and M_1 M_2 are both chords on a circle round P_4). However when working with the interferometer it is desirable to have the fringes localised in some other specified plane. (In the present investigation the fringes were localised in the arm of the interferometer between the plates P_2 and P_4). Let the fringes attain their maximum sharpness at a given distance g from plate P_4. (Fig. 3.3) To obtain this an added angular displacement of P_1 about a horizontal axis is required. This displacement will affect those light rays hitherto unaffected which are refledted from P_3. Let β be the angle through which P_1 is tilted; then S will be displaced by $2\beta f$ along the arc of radius f about P_1 towards the right and will now be at S_1'. The interfering pair of light points is thus given by S_1' S_2. Since to a first approximation the arcs of radius round P_1 and of radius $f + c$ (where $c = a + b$) round P_4 coincide in the neighbourhood of S_1' the perpendicular bisector of S_1' S_2

will again pass through P_4.

Light point M_1 however (whose distance from P_4 is also $f + c$ for simplicity) will shift to M_1' which will no longer lie on the arc $M_1' M_2$ even if angle β is small and hence the perpendicular bisector of the coherent light points $M_1' M_2$ will no longer pass through P_2. The problem is then to determine β, so that the intersection of the new bisectors of $S_1' S_2$ and $M_1' M_2$ takes plate at distance g from plate P_4 and thus sharp fringes will appear there. Denoting $S_1 \hat{P}_1 M_1$ By ψ; $S_1 \hat{P}_4 M_1$ by ϕ; $S_1 \hat{M}_2 M_1'$ by ξ. Then $P_1 \hat{M}_1 P_4 = M_1' \hat{M}_1 M_2 = \psi - \phi$ and $M_1 M_2 = 2\alpha(c + f)$; and $M_1 M_1' \doteq 2\beta f$. Further from triangle $M_1 M_1' M_2$ taking into account that angles $\alpha, \beta, \phi, \psi$ are small we have

$$\xi = \frac{\beta f (\psi - \phi)}{\alpha(c + f) - \beta f}$$

In triangle $P_4 U M_1$ we have $P_4 \hat{M}_1 U = \xi$ and the sine theorem gives

$$\frac{c + f}{g} = \frac{\phi - \xi}{\xi}$$

Further from triangle $P_1 P_4 M_1'$ ($P_1 M' \doteq f$)

$$\frac{f}{c} = \frac{\phi}{\psi - \phi}$$

Solving these three equations with respect to g gives

$$g = \frac{c}{\frac{\alpha}{\beta} - 1} \qquad (3.1.)$$

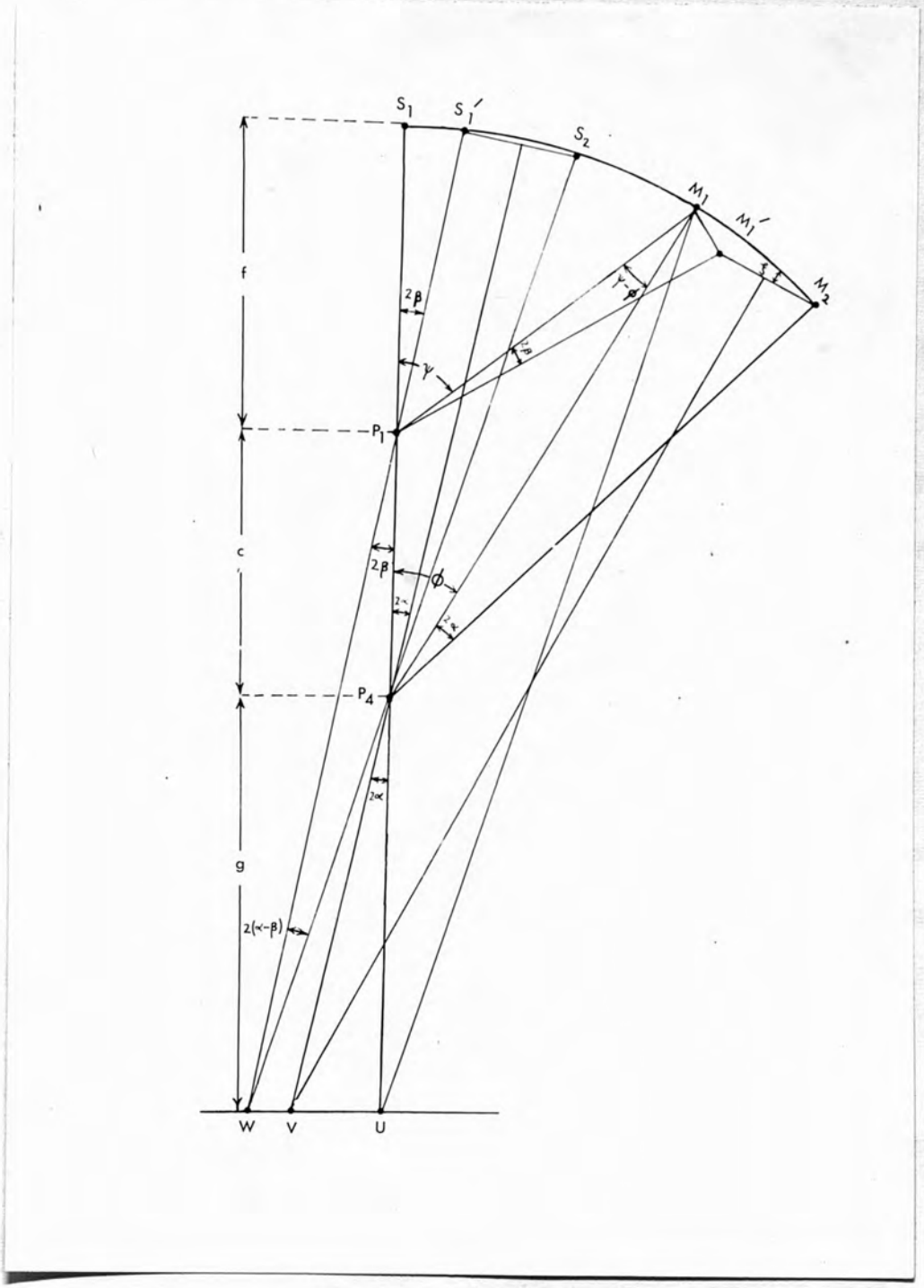

Fig. 3.3.

(i) Since the equation no longer contains ϕ and ψ the location of sharp interference fringes g is independent of the linear dimensions of the light source (ϕ and ψ were assumed small).

(ii) g is also independent of the location of the light source.

It is now apparent, that the point of intersection of the two rays into which an incident beam is divided by the interferometer and which pass through the instrument by two different paths (e.g. $W S_1'$ and $W S_2$ in fig. 3.3) will also be at distance g from plate P_2. For consider the triangle $W P_1 P_4$ ($W P_1 \simeq c + g$; $W P_4 \simeq g$).

By the sine rule

$$g = \frac{c}{\frac{\alpha}{\beta} - 1} \qquad (3.1)$$

Hansen[35] states in his paper: "The fringes are localised where rays, coming from the same point of the dividing plate and having passed through the same distance by different paths within the interferometer, intersect".

It has been shown above that this proposition is based on the fact that given an extended source of light, the perpendicular bisectors of all pairs of coherent light points will have to intersect where sharp fringes are to be obtained.

The distance between the fringes is given again by analogy with Young's fringes. (i.e. b equals the wavelength of light

multiplied by the distance of the points of coherent light from the screen, divided by the distance apart of the point images of coherent light). Thus

$$b = \frac{\lambda (f + c + g)}{2\alpha(f + c) - 2\beta f.}$$

Substituting for g and simplifying

$$b = \frac{\lambda}{2 (\alpha-\beta)} \qquad (3.2.)$$

Thus the distance of the fringes from each other depends apart from λ only on α and β .

In practice the above conclusions drawn from equation (3.1) are not strictly true and the use of a finite source does involve difficulties. All light rays from such a source can not be made parallel by a lens and so a difference in path length caused by rotation of P_4 is not the same for coherent rays incident at different angles, the interference condition is not completely satisfied so that the rays become indistinct. It was found that the contrast of the fringes was improved as the aperture in front of the source was reduced to a minimum size compatible with requirements for sufficient intensity for good photographs. Further the angular opening of the source restricts the tolerance on the thickness of the beam splitters for this reason: if a different thickness of glass exists between the two paths it can be compensated for by translation of plate P_3, but if the light rays pass through

the glass at different angles, due to angular separation of those leaving the source the optical path difference varies with this angle. Compensation can only be made for one angle and this is usually that which the central ray makes with the glass.

3.(iii) Requirements of the instrument

For the purpose of the present work there were two main requirements to be satisfied in the design of the instrument.

(i) The elimination of all vibrations which disturbed the fringes thus making any photographic record of growth proceedings almost impossible.

(ii) The basically difficult adjustment of the instrument should be made as easy as possible. In order that this should be so all degrees of freedom should be independent and the axes of rotation of the plates should all lie in the optical surfaces of these.

3.(iv) Design of the interferometer.

Bearing in mind the requirements as listed above the interferometer shewn in Fig. 3.4. was designed as follows. It was constructed in two main units each of which was mounted on a heavy steel optical bench with standard optical stands. The two units C_1 and C_2 each of which held a semi-reflecting beam splitter and one totally reflecting mirror mounted vertically above one another, were made of ½" thick brass. The circular glass plates were 2" in diameter, ⅝" thick and flat to within a tenth of a

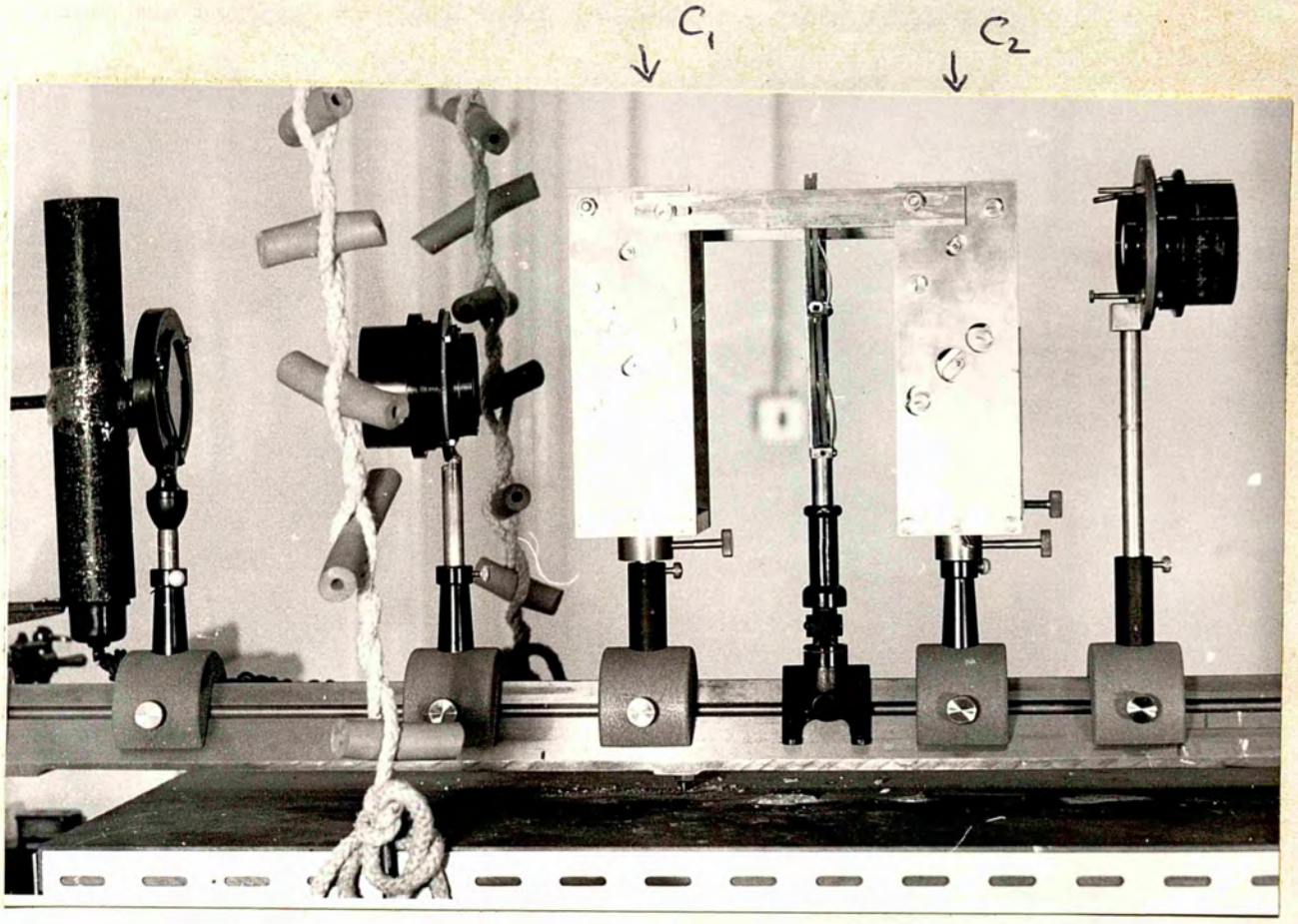

Fig. 3.4. The Mach - Zehnder interferometer showing the units C_1 and C_2 in position.

wavelength. The mirrors were aluminised and covered with a protective coating and the beam splitters were coated with multilayers of zinc sulphide and magnesium fluoride of the requisite thickness, so that the light beams had equal intensities in reflected and transmitted components. As shown in Fig. 3.5. the optical plates were mounted in heavy brass rings and supported at three points such that there was no strain which would tend to deform the optically flat surfaces in any way. Each of the plates was adjustable about two perpendicular axes one, inclined at 45° in the vertical plane, the other, horizontal. These adjustments were achieved by pivoting the heavy brass ring on two steel pins in a concentric ring which was in turn pivoted on two steel pins at right angles to the first pair, attached to the outer frame. The inner ring was pivoted about a horizontal axis. At 90° to these axes of rotation was the adjusting mechanism which consisted of a screw at one side and diametrically opposed to this screw a phosphor bronze spring giving point contact on the ring. This form of plate mounting enabled easy adjustments to be carried out about the horizontal or inclined axes. The mountings were carefully designed, as shewn in Fig.3.5. to ensure that these rotations occurred about axes lying in the optic surfaces of the plates. In addition to these rotational adjustments it was possible to translate one of the beam splitters

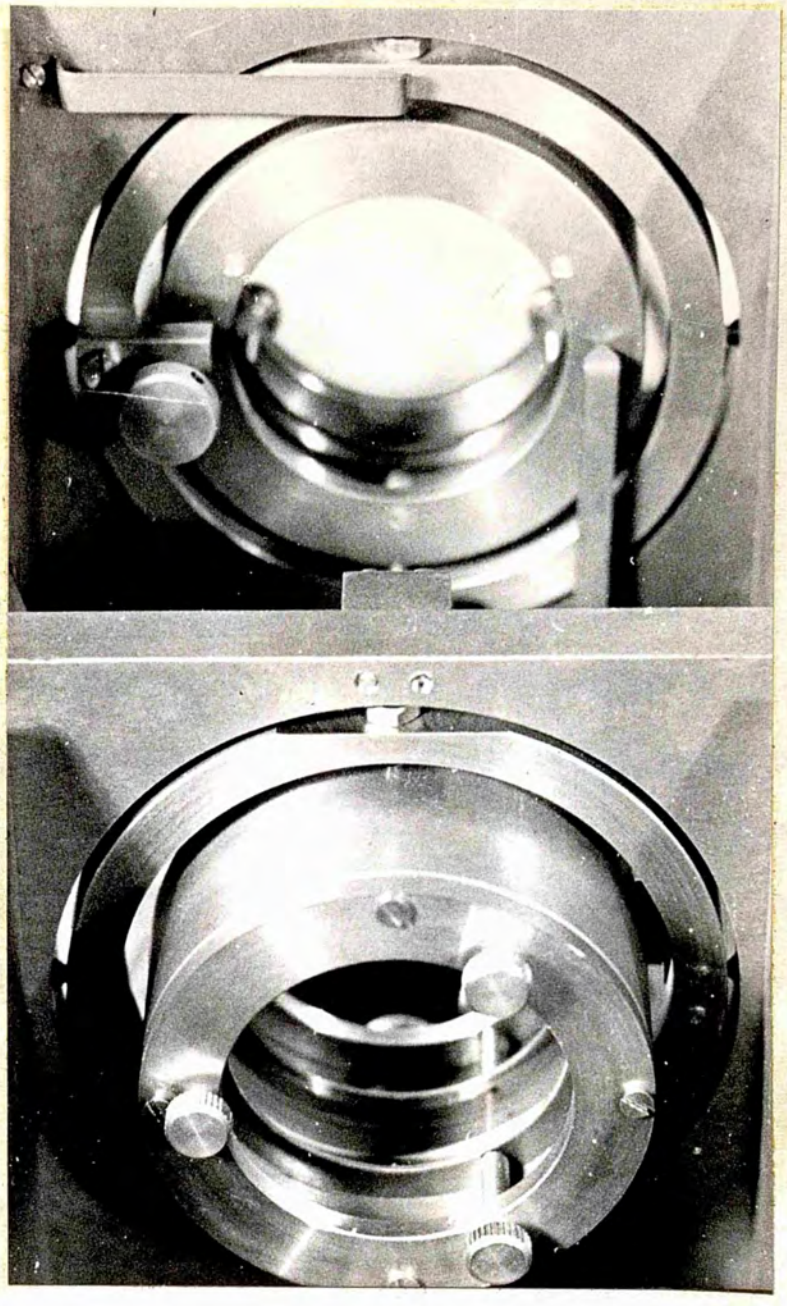

Fig. 3.5. Close-up showing the mounting for the interferometer plates.

along the axis of the instrument. A ball and slot arrangement in conjunction with a spring and a finely threaded screw allowed movement only along an accurately defined path machined in the heavy base plate of C_2. Two horizontal Dexion struts firmly connected the top of the two units C_1 and C_2 to ensure complete rigidity.

3. (v) Anti-vibration support

One of the major difficulties encountered in the use of the interferometer was the elimination of vibration, (e.g. due to heavy traffic). This was finally achieved by using an anti-vibration support similar to that designed by French [36]. This consisted of a heavy lead slab suspended from the main beams of the ceiling by means of four double ropes. These were twisted to form a series of loops within which were inserted short horizontally disposed lengths of thick rubber tubing having an external diameter of 1.6 in. and wall thickness about half an inch. Vibrations of different periods were damped out by the rubber elements and to a lesser extent by the ropes before they reached the base plate upon which the optical bench supporting the interferometer was mounted. Further refinements proved necessary and this was provided by means of viscous damping. To the frame containing the base plate were welded two metal cylinders which fitted very closely into "dashpots" containing

oil. This finally eliminated the vibration effects enabling stable fringes to be photographed.

3.(vi) Adjustment of the interferometer

This was carried out by the method due to Price[37]. The auxiliary apparatus used consisted of a small plane mirror and a pinhole of light. Fig.3.1. shows the arrangement of the interferometer with the usual ray path from source S to the viewing lens at L_2. The units C_1 and C_2 were placed the required distance apart on the optical bench. The plane mirror was mounted at B and the pinhole of light at A (Fig.3.6). On viewing at C four primary images of the light source are seen corresponding to the four possible light paths from A to B to C. The method of adjustment for fringes with monochromatic light consisted in the superposition of the plates. If the fringes were not then visible it was found with the present instrument that a further slight rotation of one of the plates or translation of the plate P_3 was successful.

The method described was slightly complicated by the presence of secondary images which resulted from multiple reflections from the dividing plates. This is due to the fact that the light rays do not traverse the same paths that they would in the normal operation of the instrument, the coating of the plates will not be optimum for minimisation of multiple reflections and for equal intensity by each light path. Consequently these secondary images were

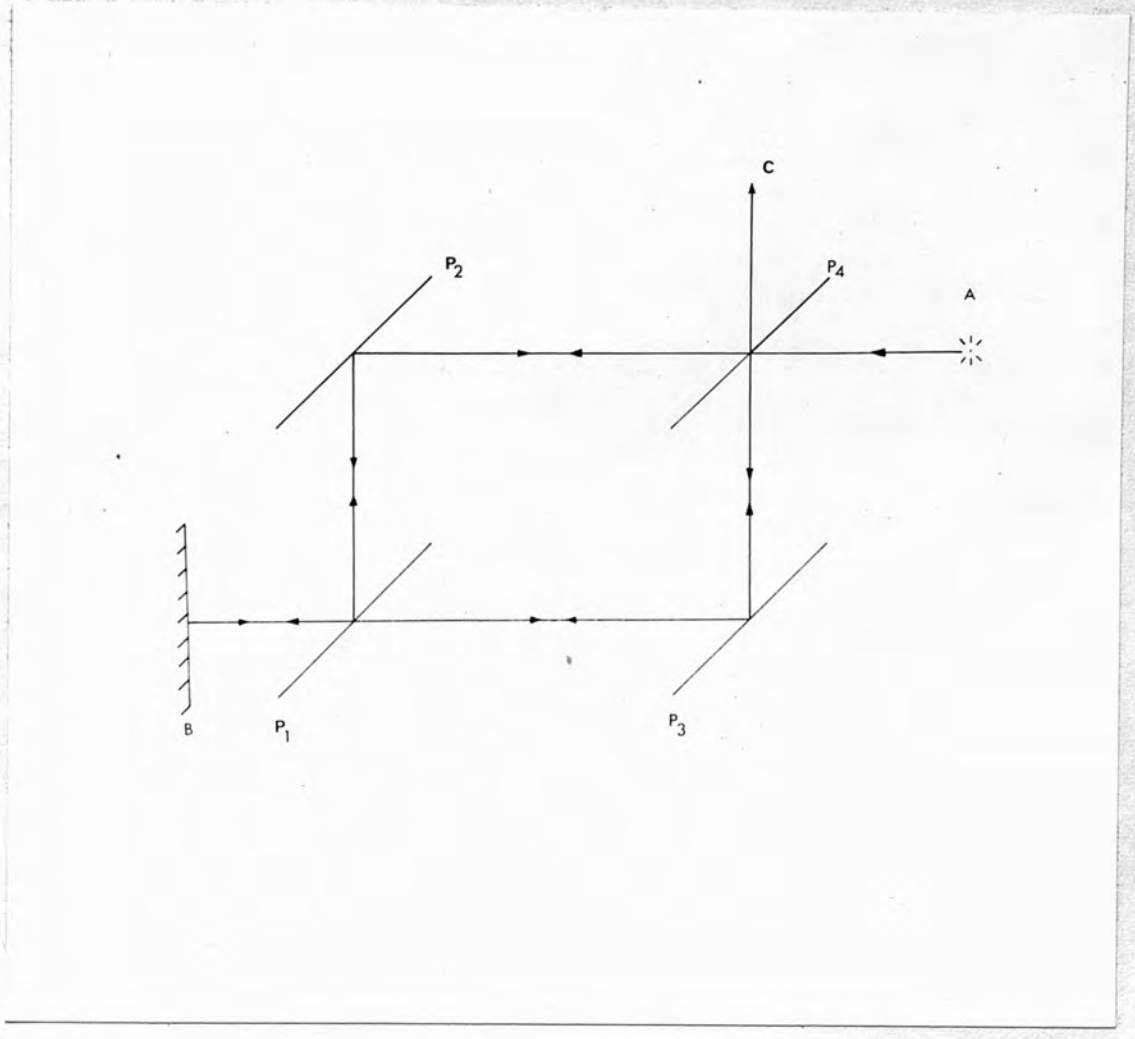

Fig. 3.6.

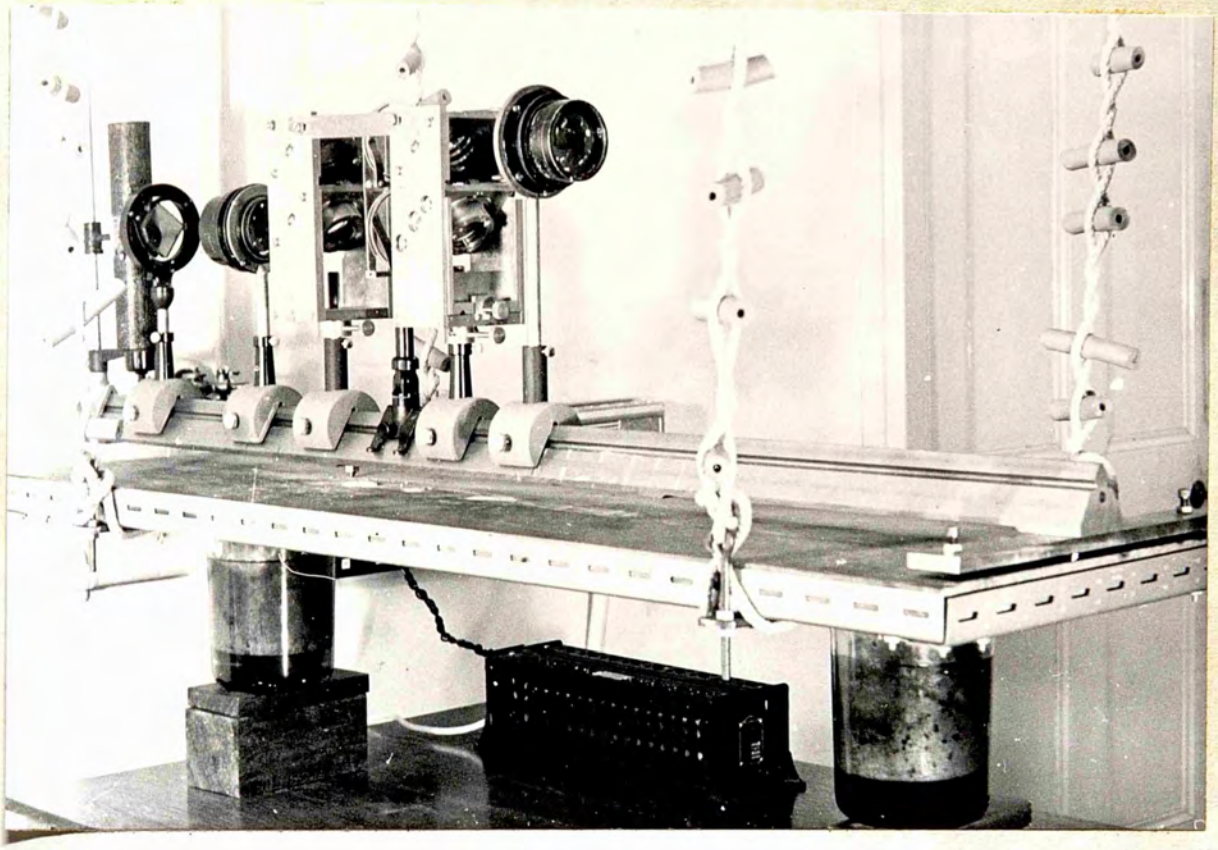

Fig. 3.7. The Mach - Zehnder interferometer and anti-vibration support.

relatively bright and often hard to distinguish from the primary ones. Four sets of images were thus produced and by rotation of the plates these moved corresponding to the four primary images and were then superimposed. The auxiliary apparatus was then removed and the source, a low pressure mercury lamp, before which was placed an adjustable aperture and a Wratten 5461$\mathring{A}$ green filter, was placed in the normal position for operation. (Fig.3.7). A condensing lens produced a parallel beam of light incident on plate P_1 of the interferometer. On viewing through plate P_4 monochromatic fringes were then seen. These were localised in the correct plane by focussing a telescope on the required position between plates P_2 and P_4. Then, with experience, it was found that by correct rotation of one of the plates, fringes could be brought into the field of view. At the appropriate moment the growing crystal was placed in the correct position so that it was in focus and translation of plate P_3 would bring the fringes back into the field of view again. The telescope was then removed and replaced by lens L_2 the position of which was adjusted so that fringes were obtained on the screen at the back of the camera.

3.(vii) Evaluation of Interferograms

Inside the interfermometer the interfering pencils of light are separated along different paths. When a medium of different refractive index is introduced into one of the arms a displacement

of the fringes results. This can be measured and allows conclusions to be drawn as to the refractive index of the medium in question. In the present work a cell containing supersaturated solution was introduced in the path of the light between P_1 and P_3 and mounted vertically above it in the arm P_2 P_4 was a cell containing the growing crystal in solution of the same supersaturation. This was necessary so that any displacement of the fringes was due to the effect of the growth of the crystal alone.

The path difference, introduced when interference fringes are formed between parallel plates is given by the formula

$$n \lambda = 2\mu t$$

for light at normal incidence.

For the Mach-Zehnder interferometer this formula becomes

$$n \lambda = \mu t$$

As the light beam passes only once through the test section.

Where n = the order of the fringe

λ = wavelength of light in vacuo

μ = refractive index of medium

t = thickness of medium refractive index μ.

If Δn is the change in the order of the fringe produced by a change in refractive index of $\Delta\mu$ due to the growth of the crystal in a cell of thickness t then

$$\Delta\mu = \frac{\Delta n . \lambda}{t}$$

$\Delta\mu$ can thus be calculated and with reference to tables showing the variation of refractive index with concentration a knowledge of the change in concentration is gained.

CHAPTER IV

SUCROSE

4. (i) Introduction

In the previous studies of conditions in the solution around a growing crystal the substance used was sodium chlorate. This is an ionic compound which forms cubic crystals.

Sucrose is entirely different in that it belongs to the group of non-polar organic compounds and is no longer of simple cubic shape.

4. (ii) The crystallography of sucrose

Crystals of sucrose belong to the monoclinic crystal system. In this system there are three unequal crystallographic axes, two of which are at right angles while the third is inclined. In the conventional orientation the c - axis is vertical, the b - axis is horizontal and runs from left to right while the a - axis is inclined downwards from back to front (Fig. 4.1a). The latter is therefore perpendicular to the b - axis, but is inclined to the c - axis. In the monoclinic system there are three classes of symmetry and sucrose belongs to the sphenoidal class which has only an axis of two fold symmetry coinciding with the b - axis. The crystallographic constants of sucrose are as as follows. - Axial ratios a: b: c = 1.2595 : 1 : 0.8782

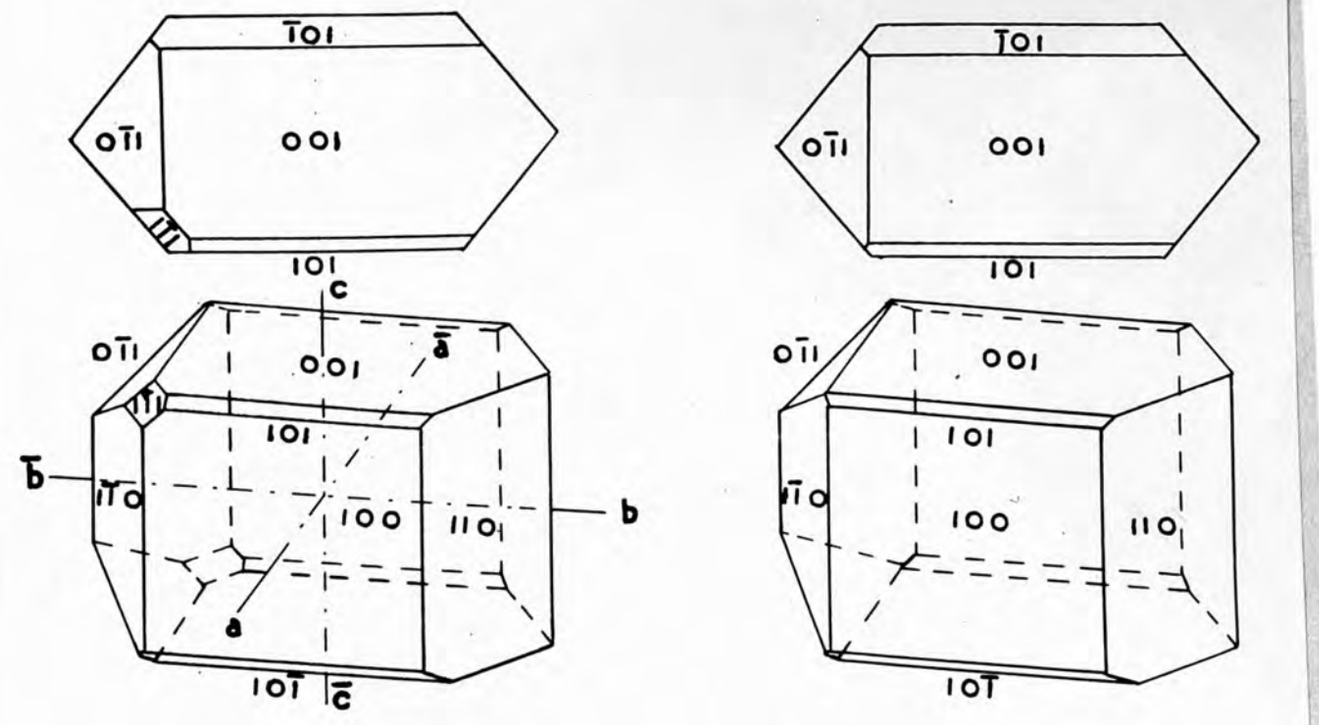
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Fig. 4. 1.

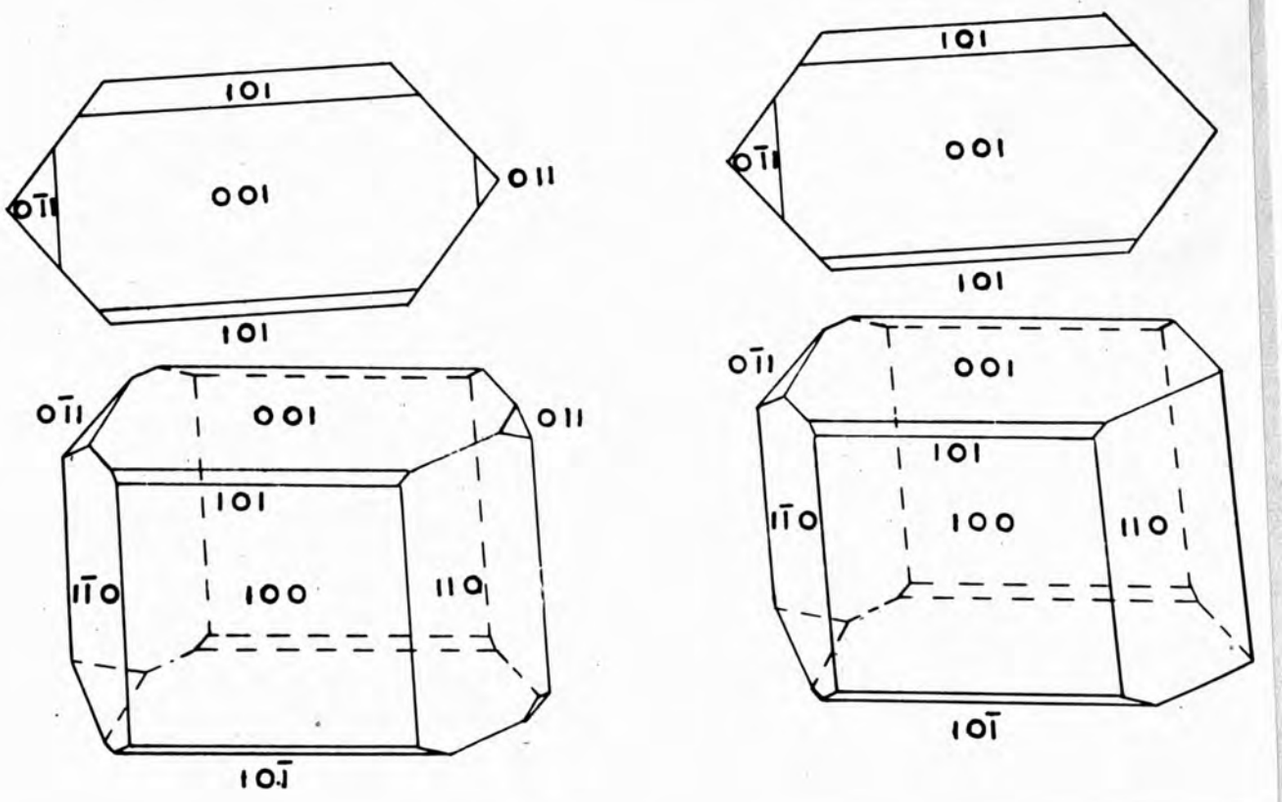
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Fig. 4. 2.

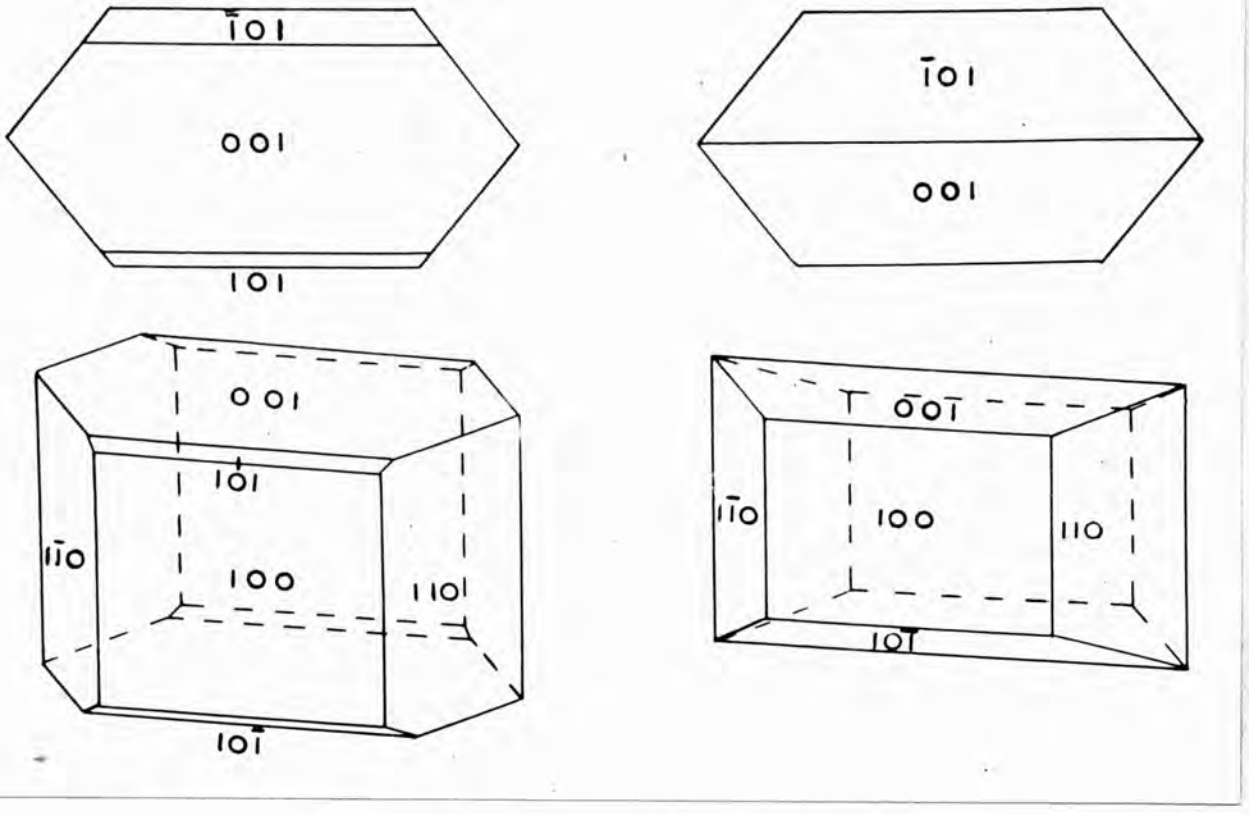
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Fig. 4. 3.

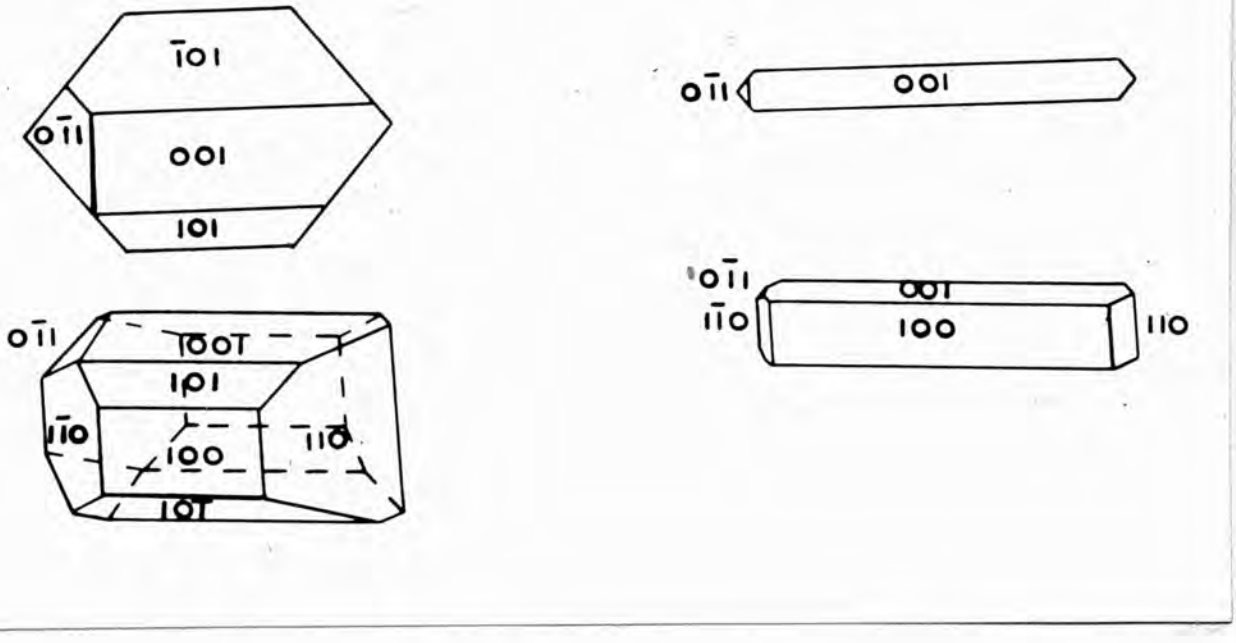
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Fig. 4. 4.

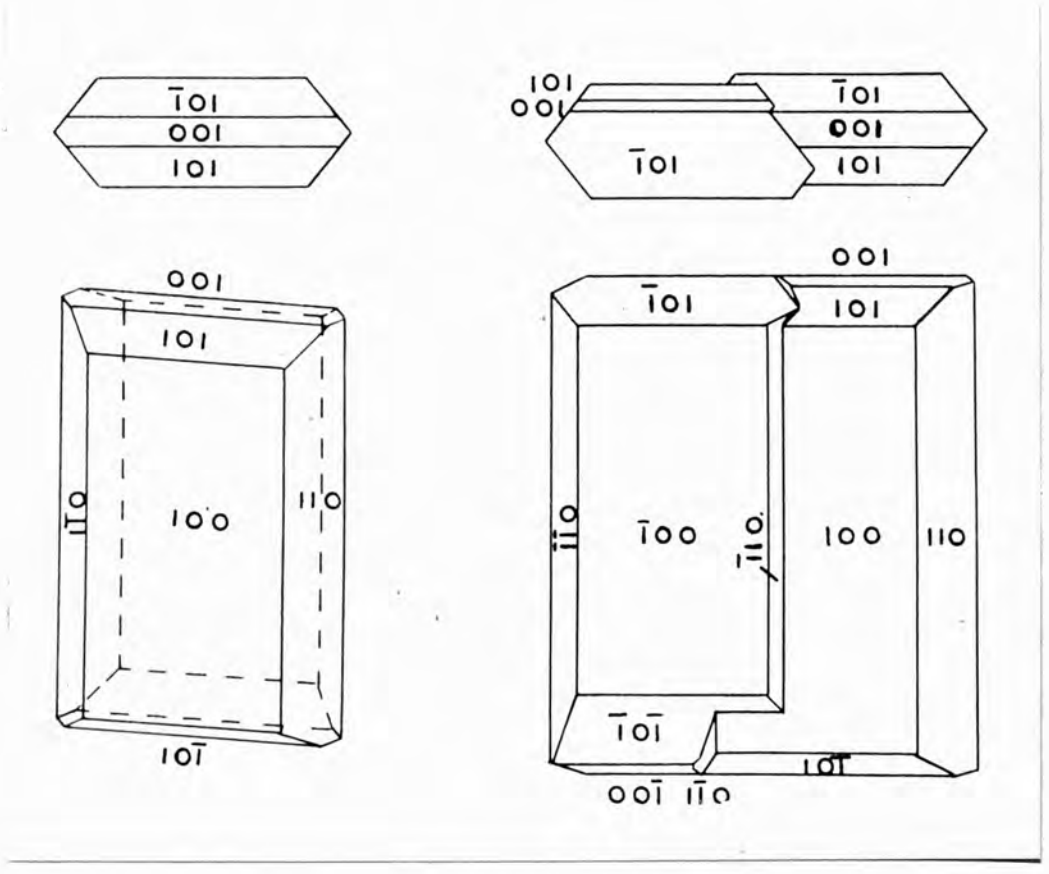
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Fig. 4. 5.

The axial angle between the a and c axes is 103° 30'
From these constants it is possible to calculate the interfacial angle between any pair of faces on the crystal.

Drawings of sucrose crystals are illustrated in Figs. (4.1 - 4.5). These represent idealised cases of various habits. The type of crystal used in the present work was mostly of habit similar to that shown in Fig. (4.3b).

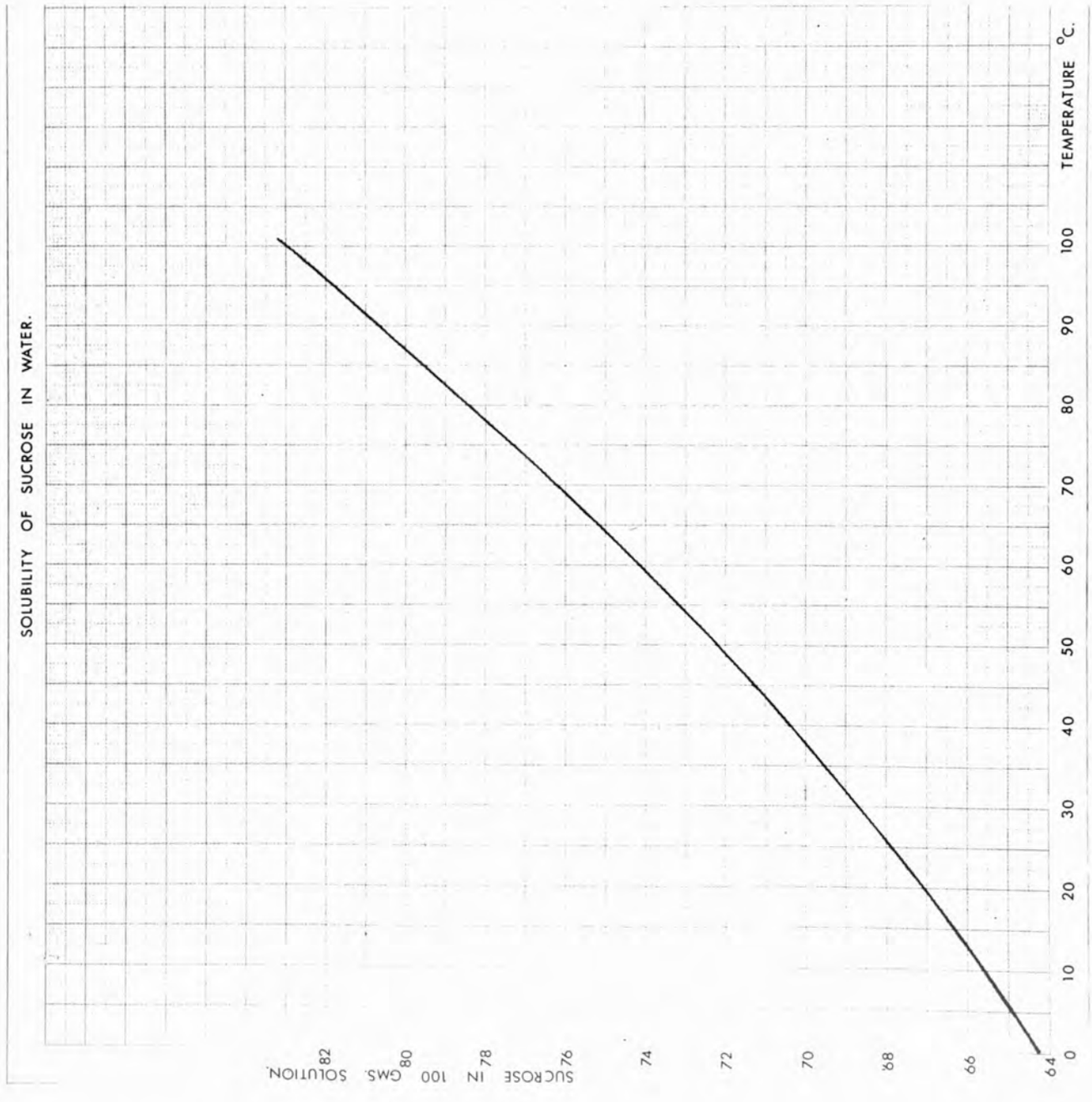
4.(iii) Growth features on Sucrose crystals.

Bunn [15] in his studies of crystals had found that layer growth was not observed on crystals of non polar substances. Since that time however layers have been observed on sucrose crystals Powers[37]. These layers were 1000 Å or more in thickness. In later work Albon and Dunning[38] also observed spiral growth showing that sucrose crystals growing from solution do sometimes exhibit the mechanism of growth from the vapour advanced by Burton, Cabrera and Frank [17].

4.(iv) Sucrose solutions

Saturated solutions of sucrose were prepared taking care to avoid spontaneous nucleation. The solubility curve for sucrose is given in fig. 4.6 and fig. 4.7 shows the variation of refractive index of the solution with concentration.

As solutions of sucrose are relatively viscous it was found convenient in the present work, as the cells were thin, to introduce


SOLUBILITY OF SUCROSE IN WATER.
SUCROSE IN 100 GMS. SOLUTION.
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76
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72
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68
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70
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TEMPERATURE °C.

FIG 4.6.

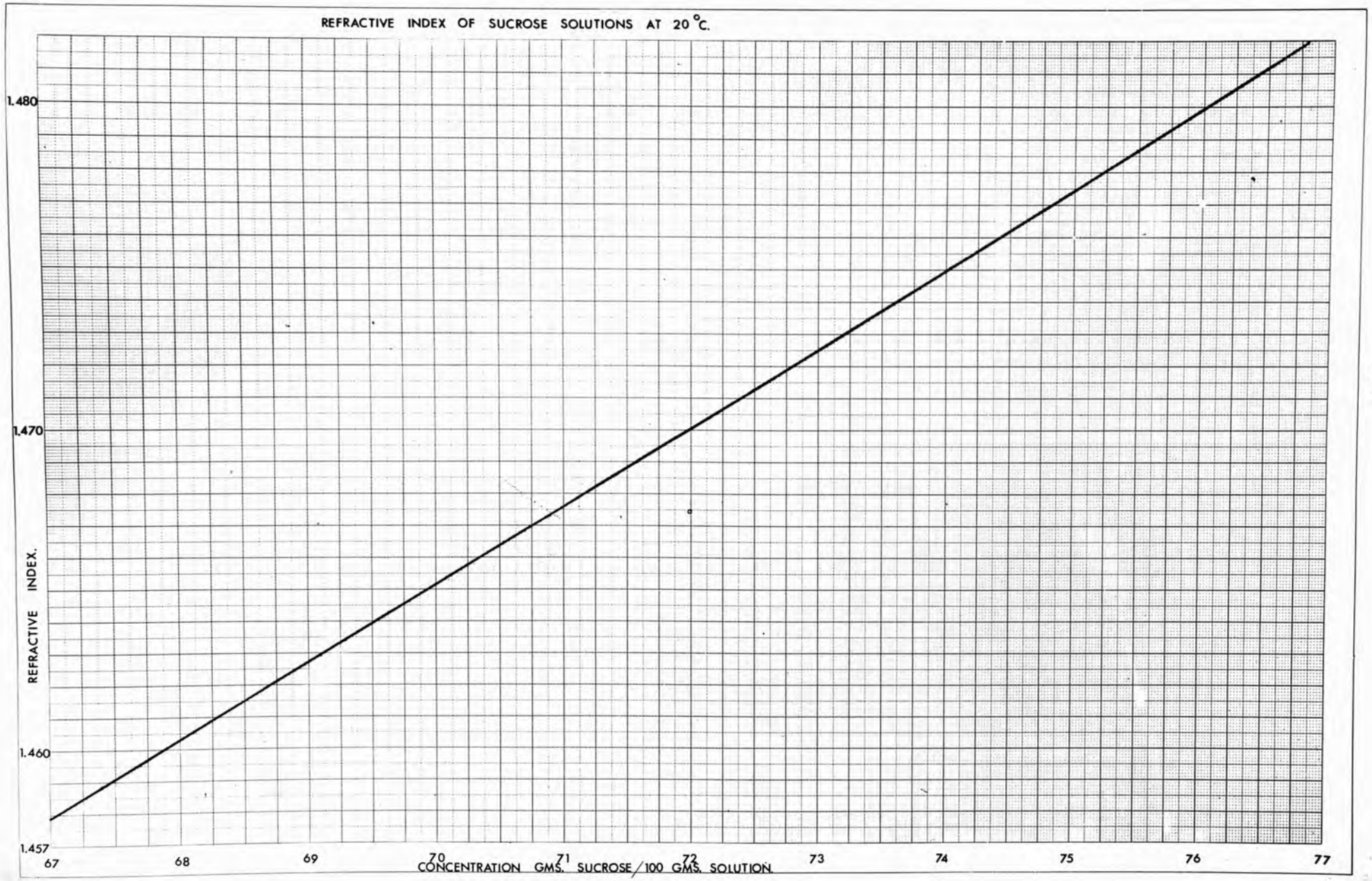

REFRACTIVE INDEX OF SUCROSE SOLUTIONS AT 20 °C.
1.480
1.470
1.460
1.457
REFRACTIVE INDEX.
67
68
69
70
71
72
73
74
75
76
77
CONCENTRATION GMS. SUCROSE / 100 GMS. SOLUTION.

Fig 4.7.

the warm solution into the cells which had already been preheated. By this method it was found that undesirable effects due to viscous flow in the solution, which caused the fringes to become highly distorted, were avoided. This did cause initial dissolution of the crystal and a corresponding change in concentration of the initial solution but in the present qualitative work this need not be taken into account.

4.(v) Experimental details

The crystals to be grown were placed in parallel sided cells which were made from specially selected circular glass plates. The plates were 3½" diameter and the cells were formed by separating two plates with an O-ring sealed with adhesive to ensure that they were watertight. The separation of the cell walls was then approximately 0.2 cms.

Previously grown crystals supplied by Tate and Lyle Limited were then selected and mounted in the cells. In the earlier work natural crystals were mounted such that growth was limited, on the (100) faces of the crystal, by the cell walls. Later on in the work in order to try and simplify the analysis to a certain extent the $\{001\}$ and $\{10\bar{1}\}$ forms were removed by grinding the crystal which was then mounted such that the ground faces were limited by the cell walls and growth was possible on the remaining $\{110\}$ $\{100\}$ and $\{1\bar{1}0\}$ forms. In this way fringes could be formed such

that they were along or perpendicular to the growing face giving an indication of the concentration gradients existing there.

After preparation the cell containing the crystal growing in solution and an identical cell containing only solution were then mounted vertically above one another in the separate light paths of the interferometer. The instrument was adjusted to obtain fringes of good contrast and desired orientation, localised in the plane of the growing crystal.

CHAPTER V.

GROWTH OF NATURAL CRYSTALS

The results obtained for the growth of natural crystals of sucrose are here described.

These crystals were mounted such that both the (100) faces were limited by the cell walls. On looking at the photographs e.g. Fig. 5.1.1. the mottled area in the centre of the crystal is the (100) face when the crystal is viewed from the front as in Fig. 4.1a. As this is the case the dark area surrounding the (100) face consists of the sloping (1 $\bar{1}$ 0), (0 0 1) (1 1 0) and (1 0 $\bar{1}$) faces. The perimeter of the crystal seen in the photograph is therefore in reality the edges where faces, such as the (0 0 1) and ($\bar{1}$ 0 1) for instance, meet. This means that with the crystal in this position no values for the concentration at a face or the concentration gradients contiguous to a face can be calculated.

The concentration at certain positions along the edges has been calculated in a number of cases but the interpretation of this is difficult.

Throughout this chapter the crystals are labelled ABCD in a clockwise direction, A, being the top left hand corner.

Throughout these experiments the solutions were made up to an approximate concentration, (with reference to the solubility

curve), and the refractive index was then measured using an Abbé refractometer. By this means, μ_o, the refractive index of the bulk of the solution round the growing crystal can be estimated to an accuracy of 0.0002. This is as high as is warranted by the ordinary methods of temperature control and was sufficient for the present investigation. The concentration can then be determined more accurately from the graph. (FIG 4.7)

Fig. 5.1.1. Growth after – Hrs. 20 Mins. x 25

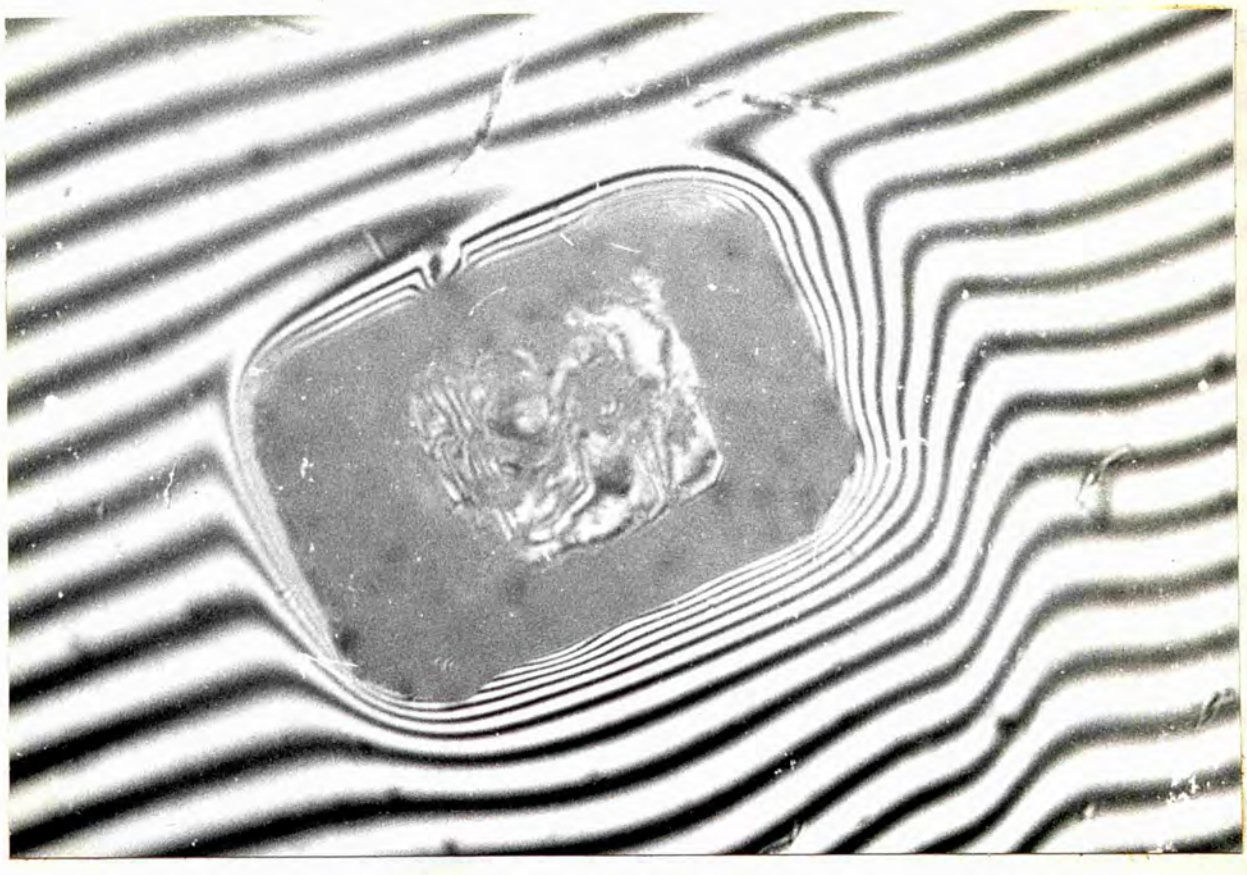


Fig. 5.1.2 Growth after ~ Hrs. 21 Mins. x 25

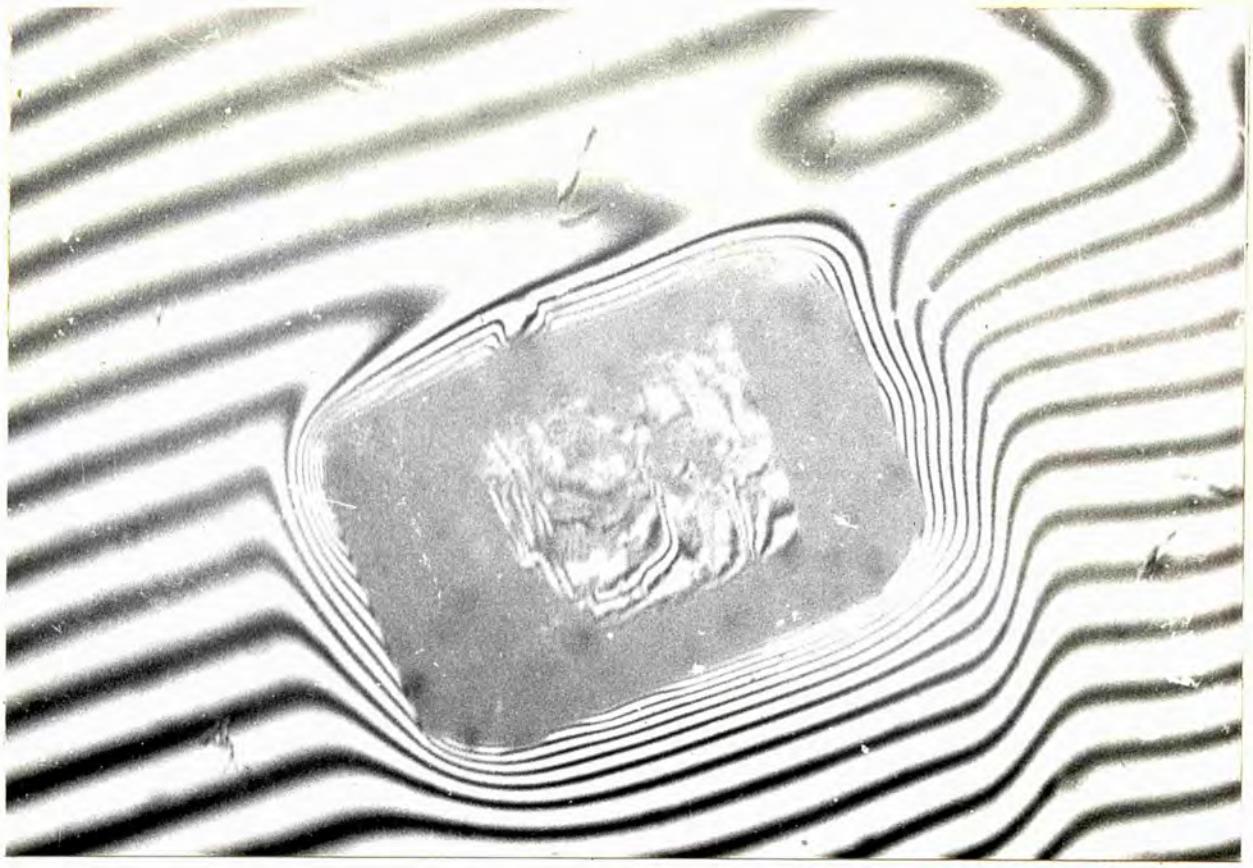


Fig. 5.1.3. Growth after — Hrs. 35 Mins. x 25

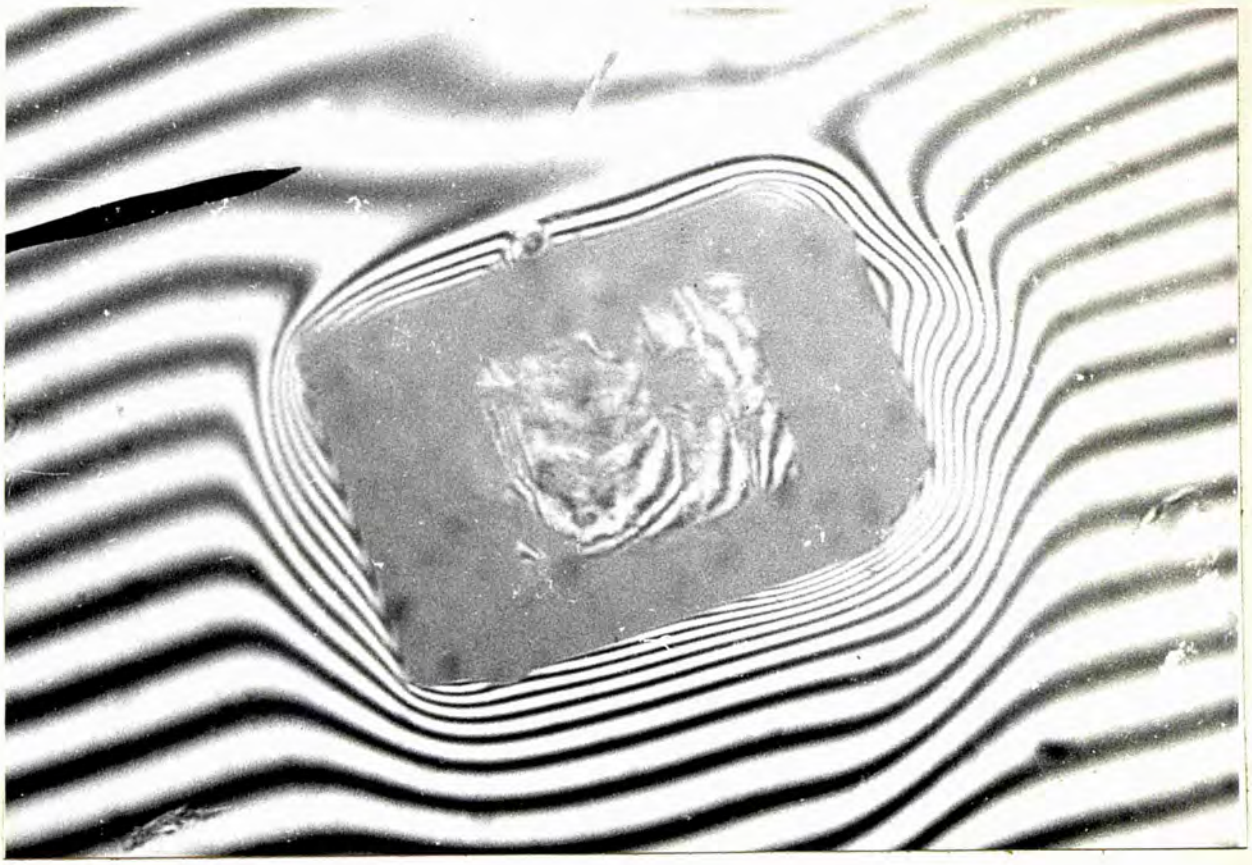


Fig. 5.1.4. Growth after ~ Hrs. 53 Mins. x 25

Fig. 5.1.5. Growth after 1 Hrs. 2 Mins. x 25

Fig. 5.1.6 Growth after 1 Hrs. 17 Mins. x 25

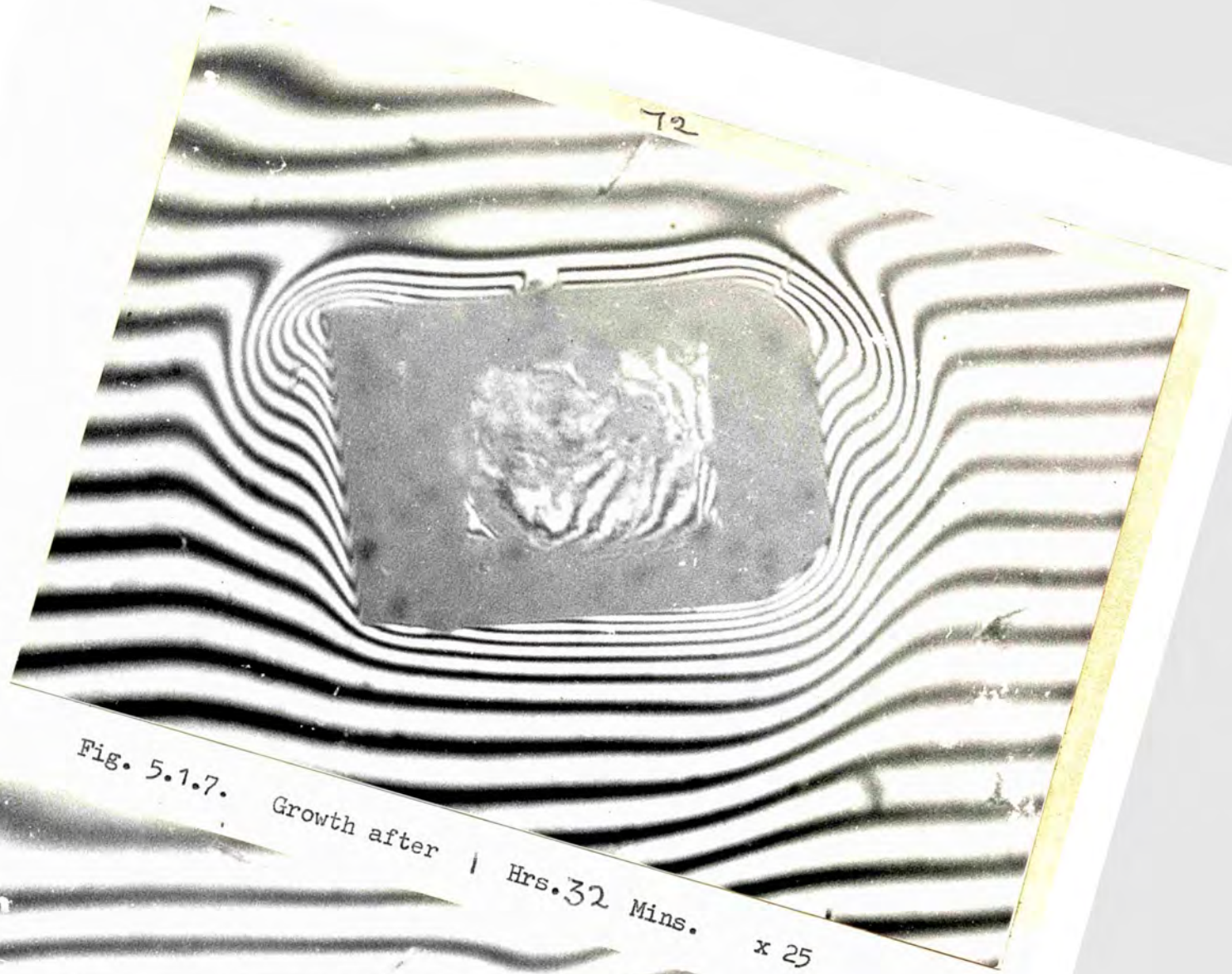


Fig. 5.1.7. Growth after 1 Hrs. 32 Mins. x 25

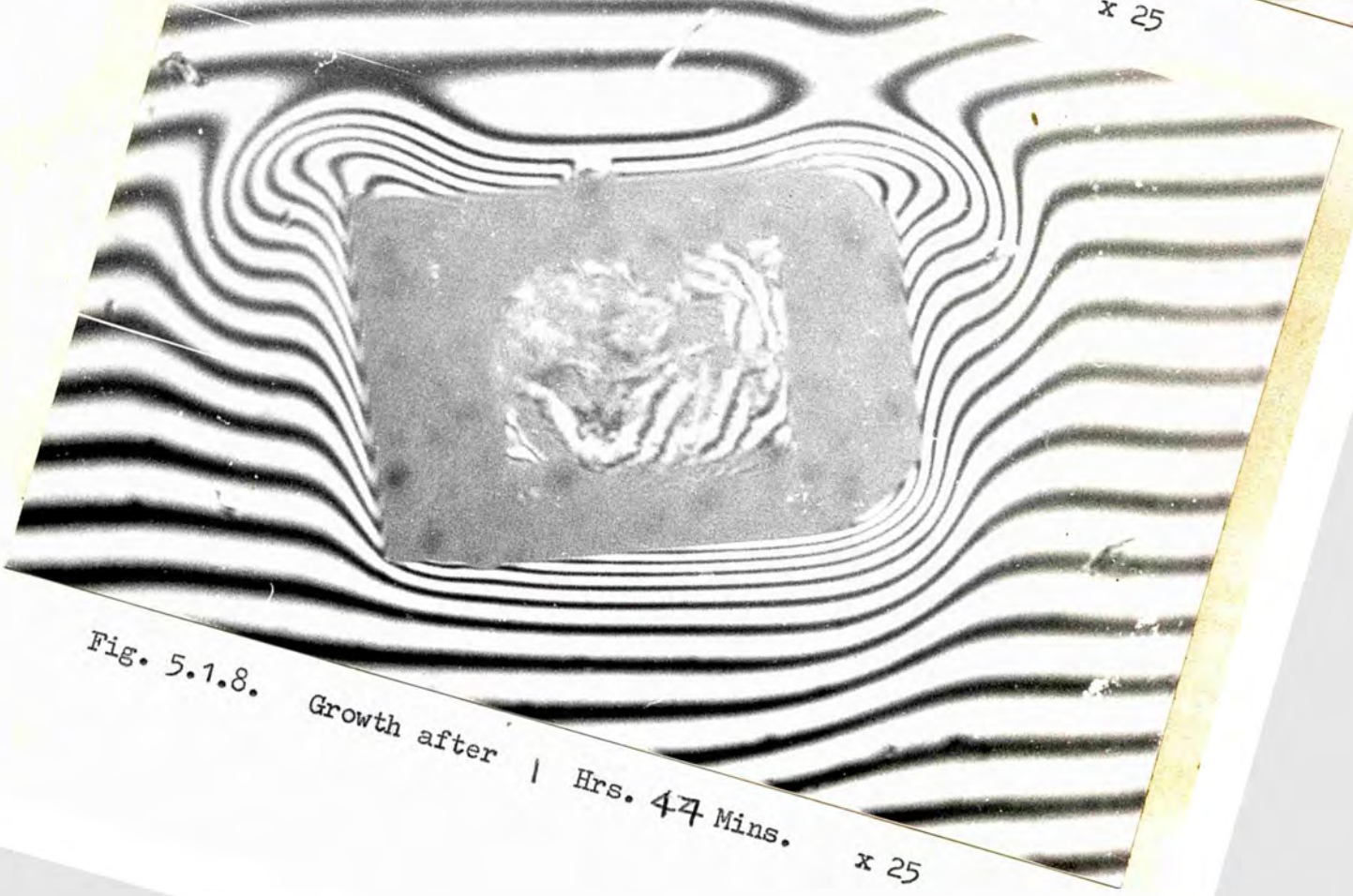


Fig. 5.1.8. Growth after 1 Hrs. 47 Mins. x 25

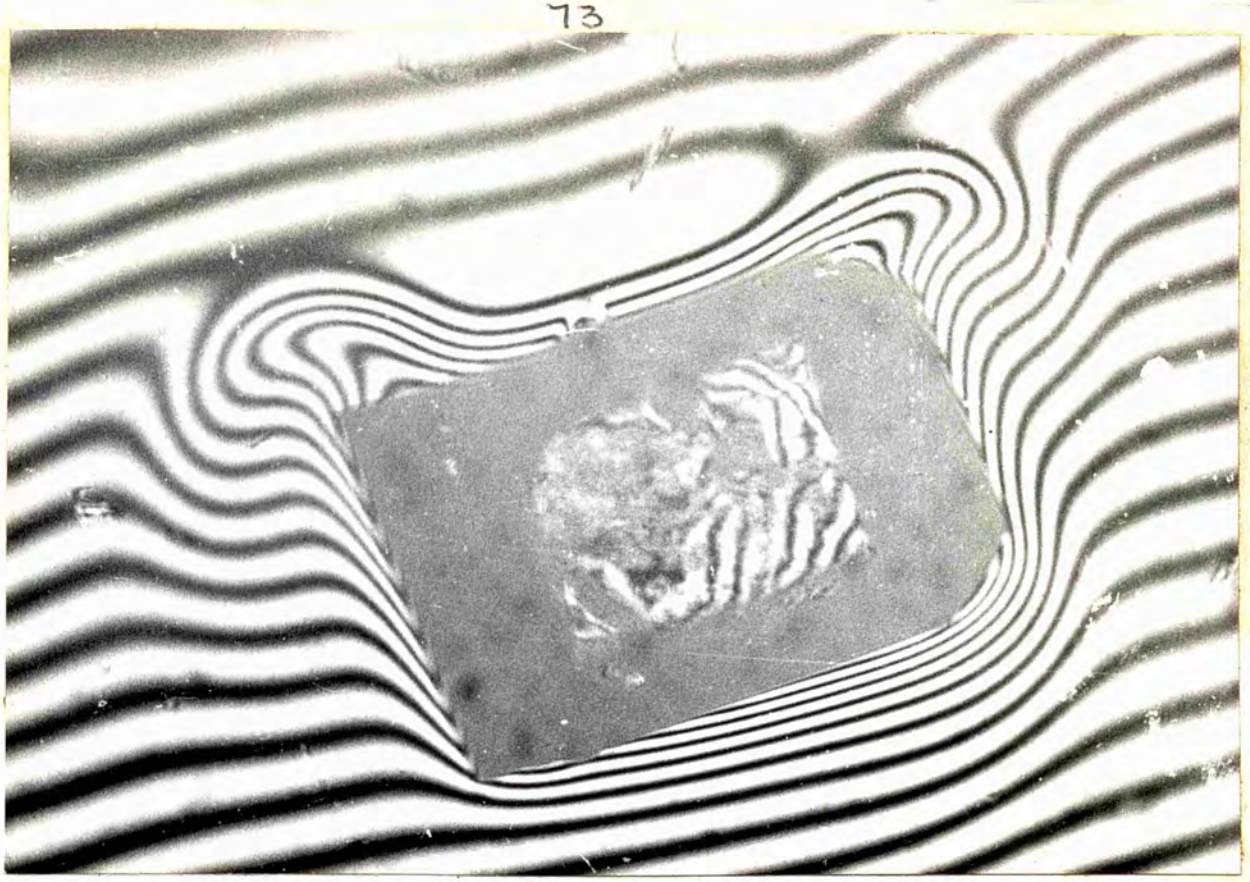


Fig. 5.1.9. Growth after 2 Hrs. 16 Mins. x 25

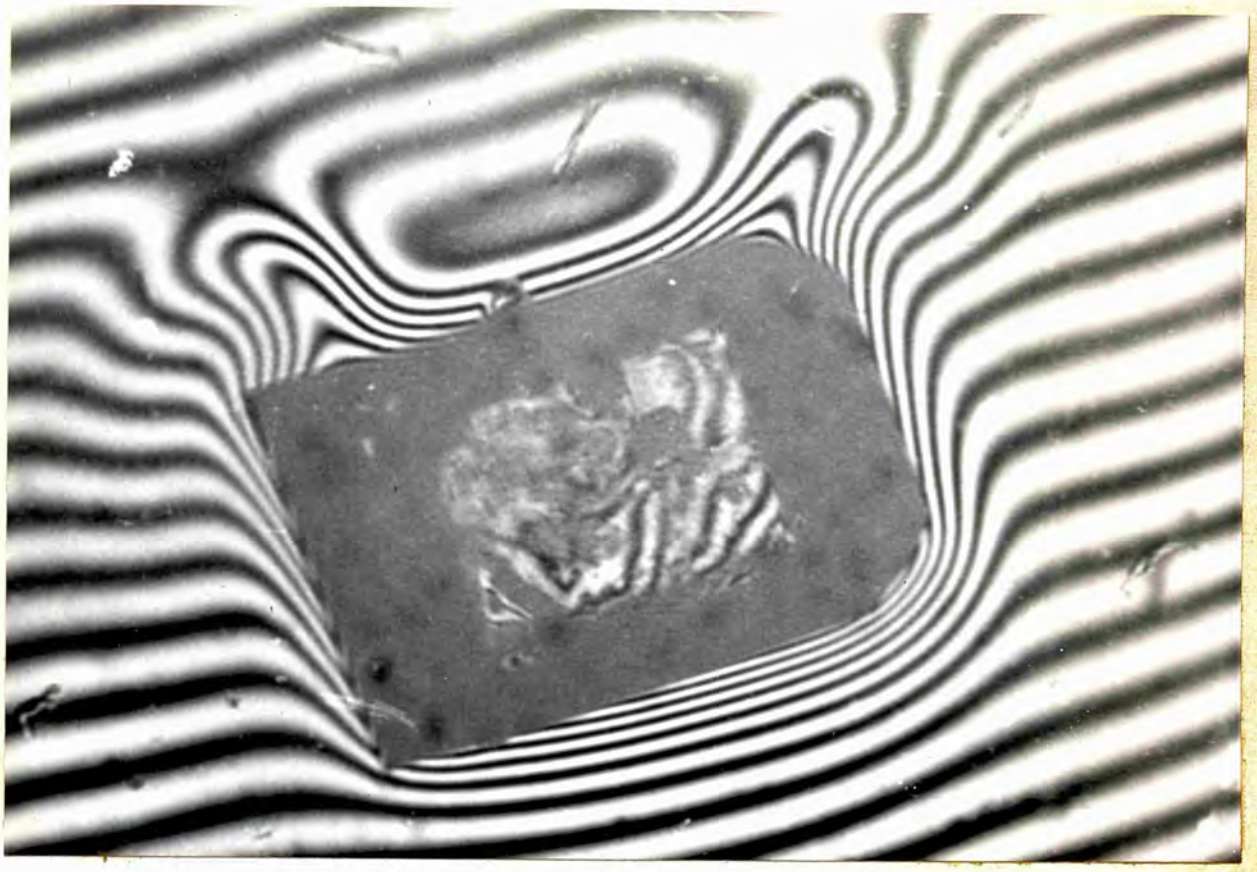


Fig. 5.1.10. Growth after 2 Hrs. 44 Mins. x 25

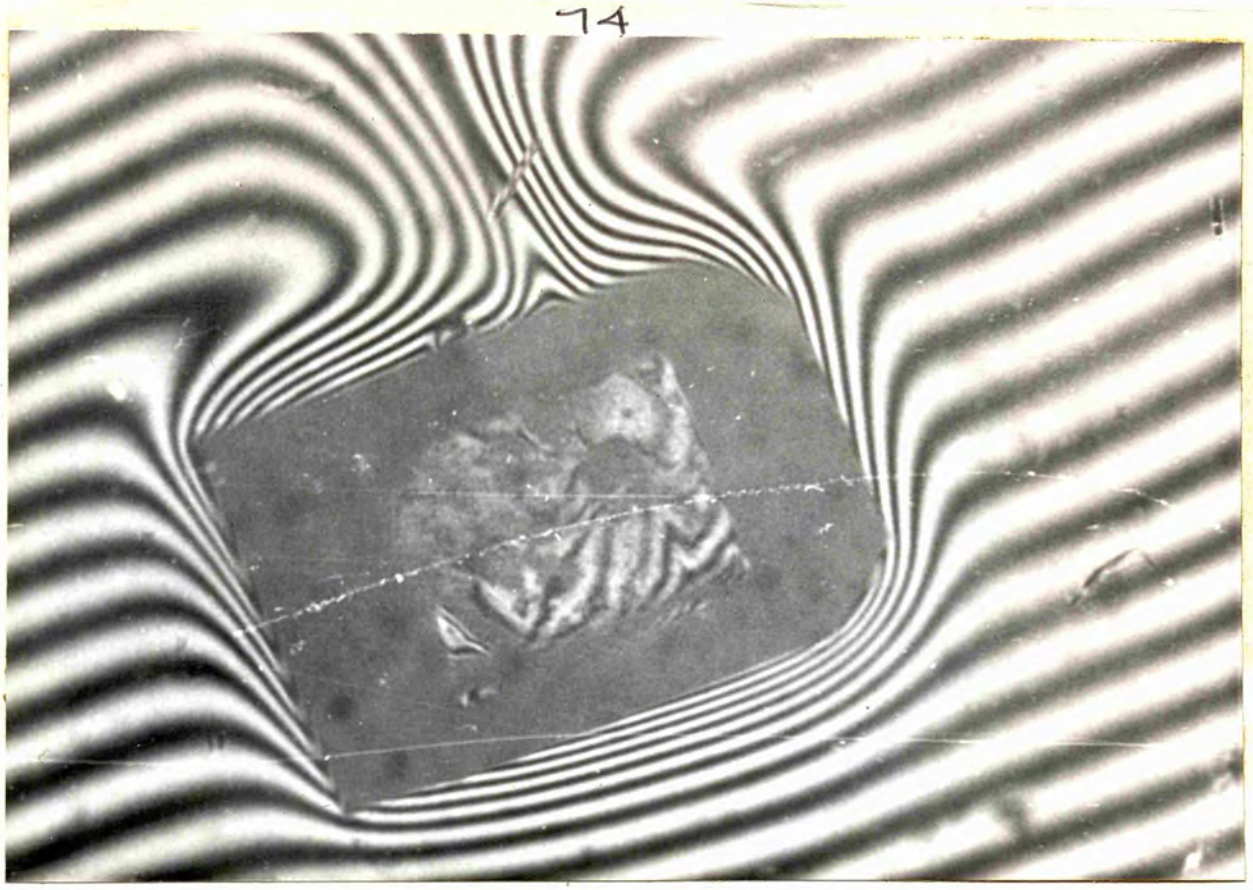


Fig. 5.1.11. Growth after 3 Hrs. 32 Mins. x 25

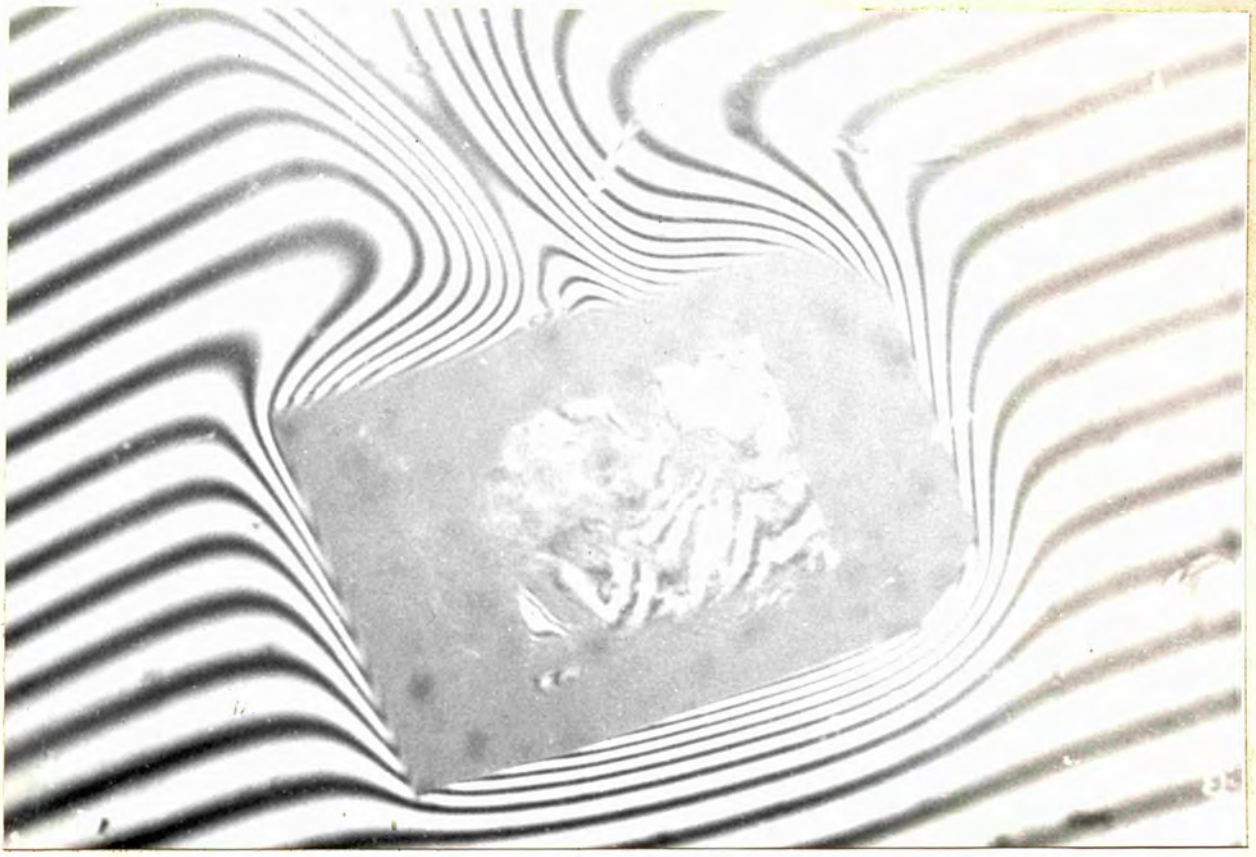


Fig. 5.1.12. Growth after 4 Hrs. 39 Mins. x 25

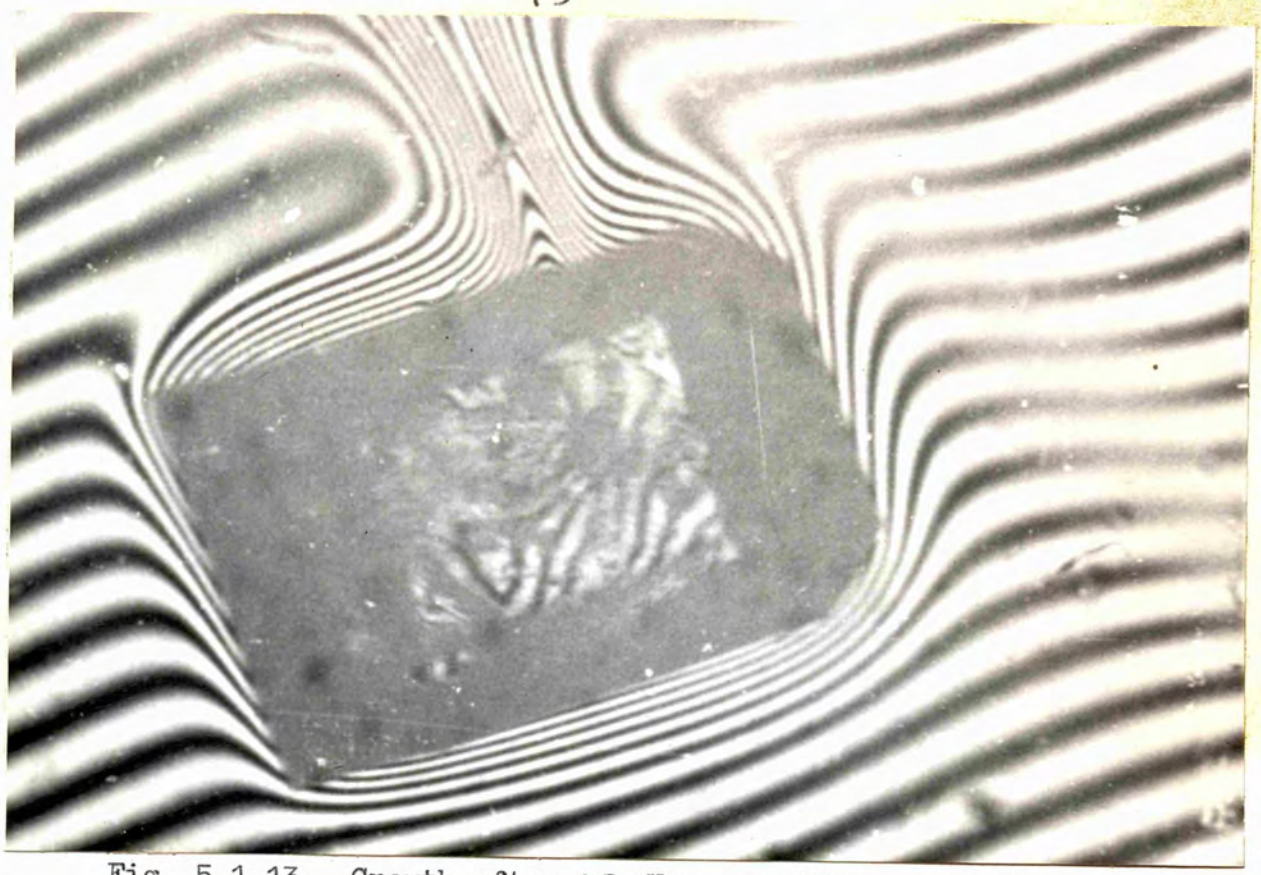


Fig. 5.1.13. Growth after 18 Hrs. — Mins. x 25

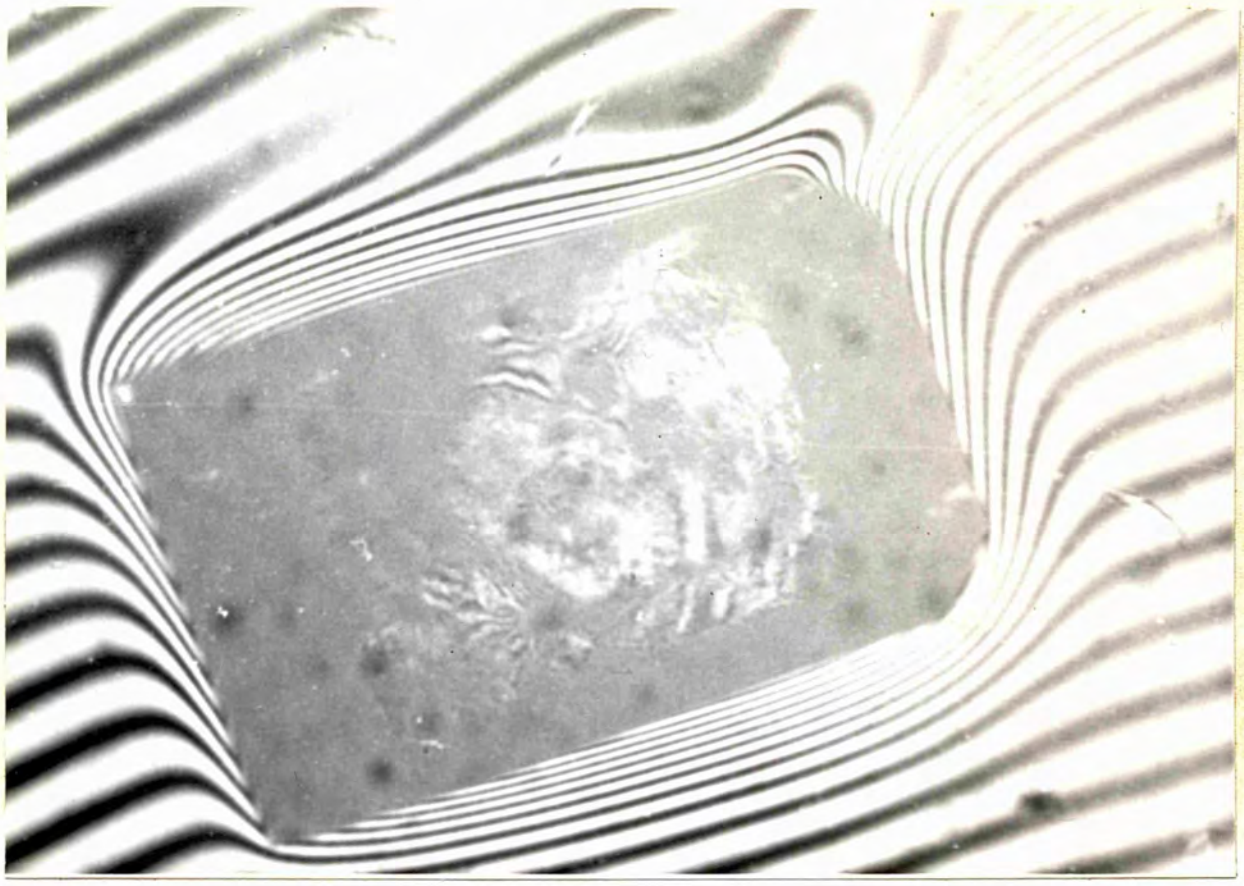


Fig. 5.1.14. Growth after 42 Hrs. — Mins. x 25

Crystal 1.

The initial concentration of the solution was 71.4%. (i.e. 71.4 gms. sucrose per 100 gms. of solution).

The various stages in the process of growth can be seen in Figs. 5.1.1. - 5.1.14. The fringes in the field of view are everywhere straight and parallel, except close to the crystal where changes occur due to the concentration gradients and the effects of convection round the crystal. Where a gradient occurs the fringes are closer together, the steeper the gradient the narrower the fringe spacing. In this investigation the concentration gradients have been estimated only qualitatively. In order to determine these accurately a great deal of computation would be necessary and this was not thought to be justified in this experiment which would need to be refined to a large extent.

The calculations of the concentration along the edges or faces of the crystal proceeded as follows.

For the parallel sided cell, of constant thickness t, in which the crystal is growing we have the formula

$$n\lambda = \mu t$$

as previously defined, and on differentiating this we have

$$\Delta\mu = \frac{\lambda}{t} \cdot \Delta n$$

Thus if the change in fringe order Δn can be estimated, $\Delta\mu$ can be calculated. It must be remembered that the fringes are actually

formed by two plates of the interferometer being inclined to one another to form a wedge. The effect on the fringes due to the growth of the crystal is superposed on the basic fringe pattern due to this wedge. Therefore in estimating the above Δn, which is the change in fringe order due to the growth of the crystal alone, a correction must be made for the dispersion of the wedge. For example in Fig. 5.1.2. at a distance from the crystal in the bulk of the solution there are 2 fringes in 1.6 cms. At the lower face CD there are 8 fringes in 1.6 cms. (measured perpendicular to the face). Thus the change in order Δn is equal to 6.

It must be remembered that the concentration gradient is a vector quantity and therefore the direction in which it is acting must be taken into account when interpreting the fringes.

For the faces BC and AD which are perpendicular to the fringes Δn is easily calculated. If the crystal had not been there the fringes would have continued undeviated. However they are diverted and Δn is the number of fringes that the undeviated fringe intersects when it is produced along its original path to the crystal face, e.g. Δn is equal to 5 at the mid point of AD in Fig. 5.1.1.

This set of photographs shows the pattern of events which was generally observed with the crystal in this position. In the

first picture taken 20 mins. after the beginning of the experiment concentration gradients can be observed around the crystal. These are such that the concentration at the edges is approximately 0.7% less than in the bulk of the solution. To the right hand side of the crystal along face BC there is a slight distortion of the fringes. In Fig. 5.1.4. a similar effect can be seen along AD and that along BC has become more pronounced.

This effect develops on both sides of the crystal until in Fig. 5.1.7 1 hour 32 mins. after the commencement of growth distinct "lobes" at the corners A and B are seen to be forming. The concentration at these two corners is then a minimum having a value of 70.5%. The reason for this ~~is~~ may be that as the crystal grows and depletes the solution contiguous to the face the less dense solution is rising up both sides and being replaced by fresh solution. The result on the fringes being seen where the less dense solution is trying to rise upwards. When the "lobes" have reached the corners A and B they do not rise immediately but move along the face towards each other. In Fig. 5.1.11. they have joined together and streaming of the solution upwards takes place from a position near the face centre. This took place within half an hour after photograph Fig. 5.1.10. but unfortunately was not recorded at the precise moment.

The solubility concentration is 67.09% so that the

concentration at the face never falls to this value. Even in the centre of the upward stream when this is established, the lowest measured value of the concentration is 70.4%. (Fig. 5.1.13.) In Figs. 5.1.11 and 5.1.12 the values are 70.75% and 70.6% respectively.

Once the stream has been established it is observed to move across the face and in Fig. 5.1.12 it has taken up a position slightly to the left of that in the previous photograph. In Fig. 5.1.13 it has moved to the right again and in Figs. 5.1.14, which shows the final stage of growth observed, the streaming is taking place from the corner.

Table 5.1. shows the concentration at the face for different values of the change in fringe order Δn.

TABLE 5.1.

t = 0.176 cms.
μ_o = 1.4685
λ = 5461 Å

Δn	$\Delta \mu$	Refractive index at the edge μ.	Concentration at the edge
3	0.0009	1.4676	71%
3.5	0.0010	1.4675	70.95%
4	0.0012	1.4673	70.87%
5	0.0015	1.4670	70.75%
6	0.0018	1.4667	70.63%
7	0.0021	1.4664	70.5%
8	0.0025	1.4660	70.4%

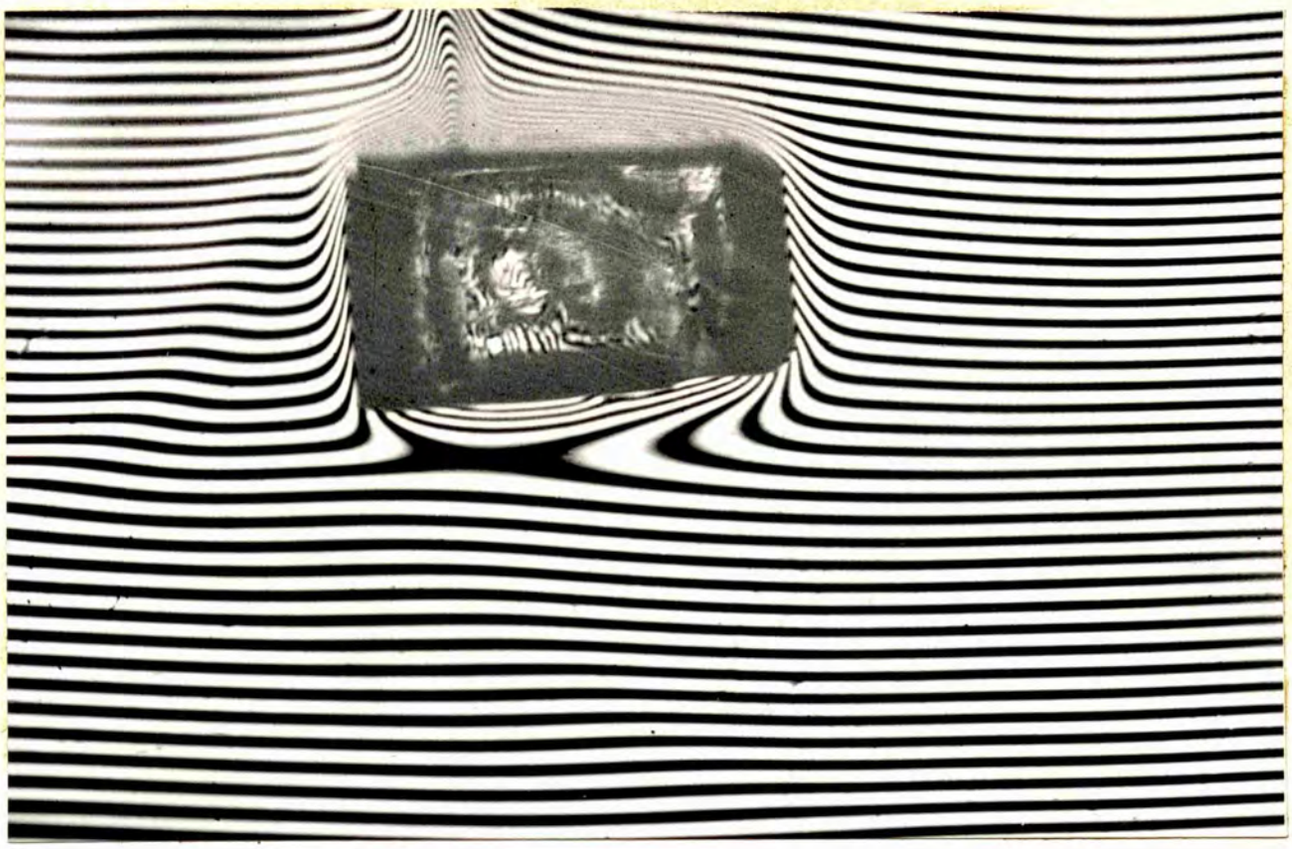


Fig. 5.2.1. Growth after – Hrs. 6 Mins. x 17.5.

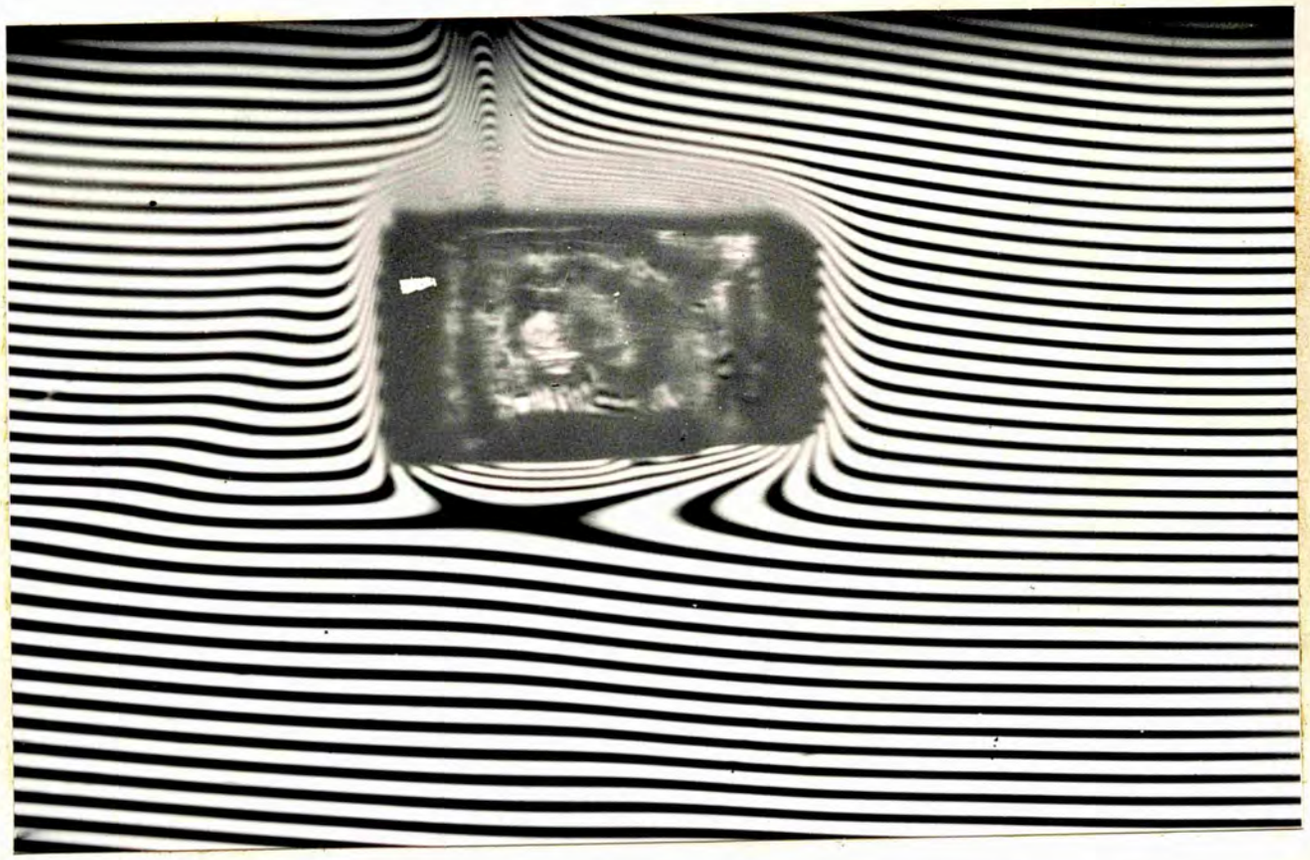


Fig. 5.2.2. Growth after – Hrs. 7 Mins. x 17.5.

Fig. 5.2.3. Growth after — Hrs. 10 Mins. x 17.5.

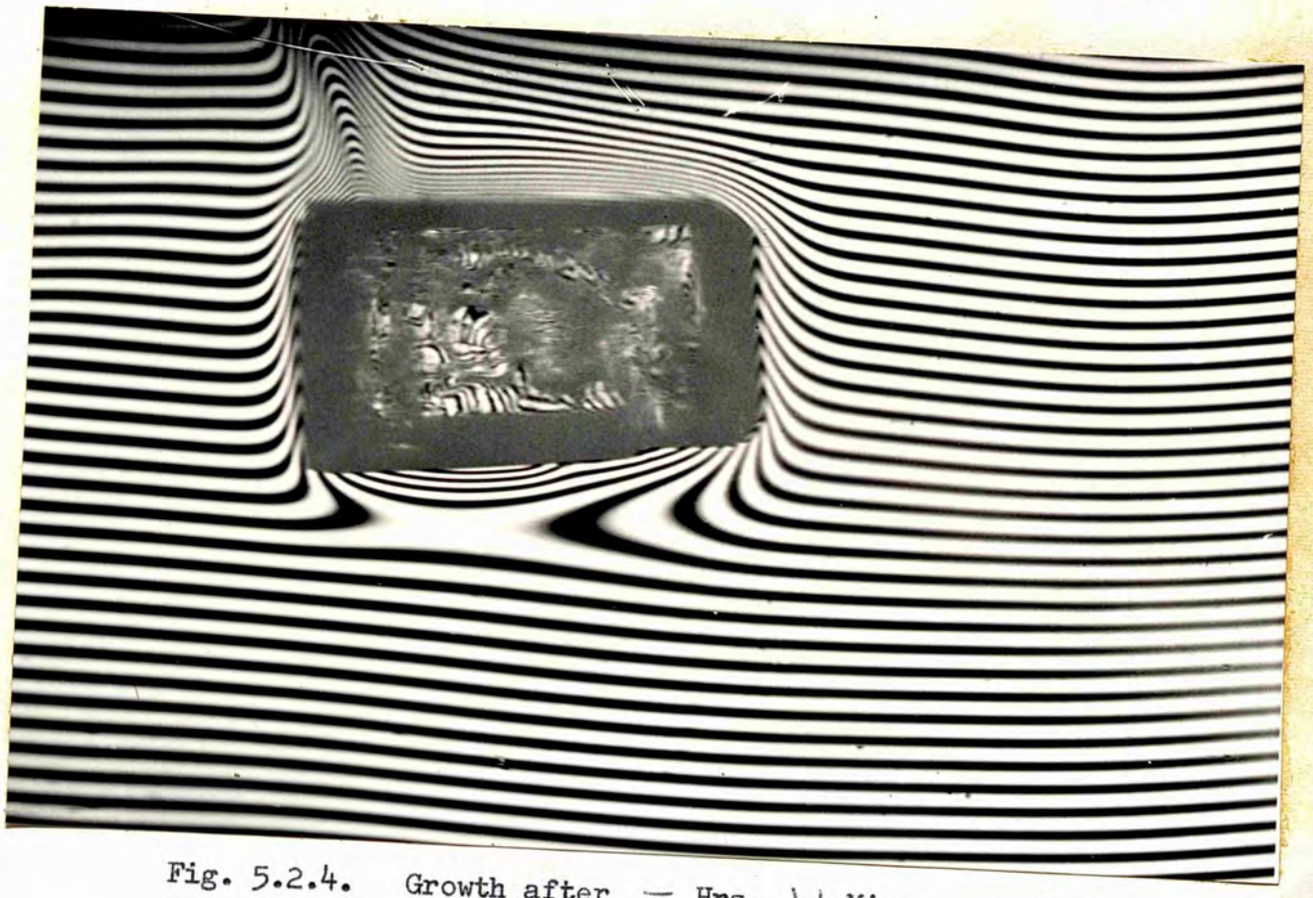


Fig. 5.2.4. Growth after — Hrs. 11 Mins. x 17.5.

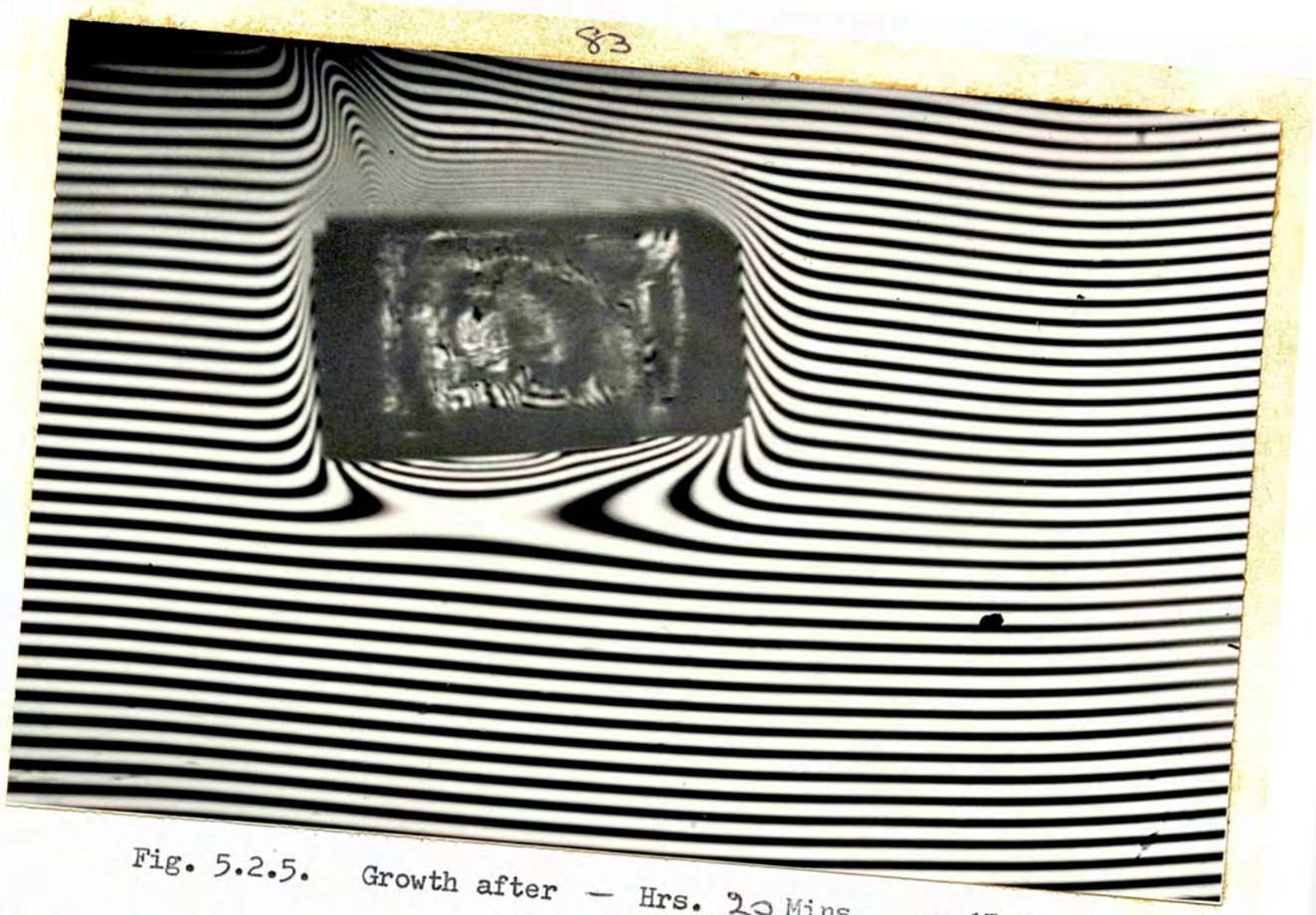


Fig. 5.2.5. Growth after — Hrs. 20 Mins. x 17.5.

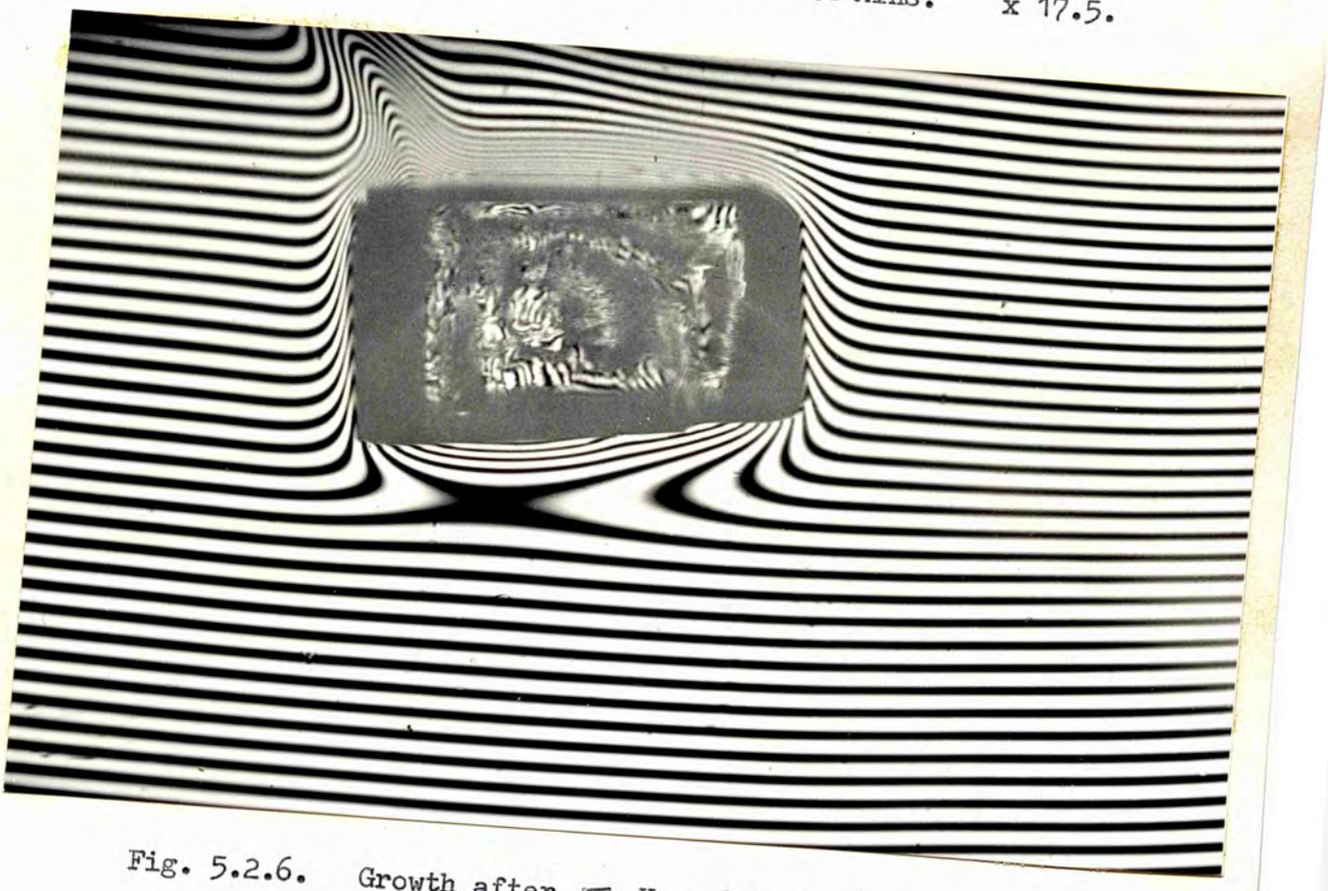


Fig. 5.2.6. Growth after — Hrs. 22 Mins. x 17.5.

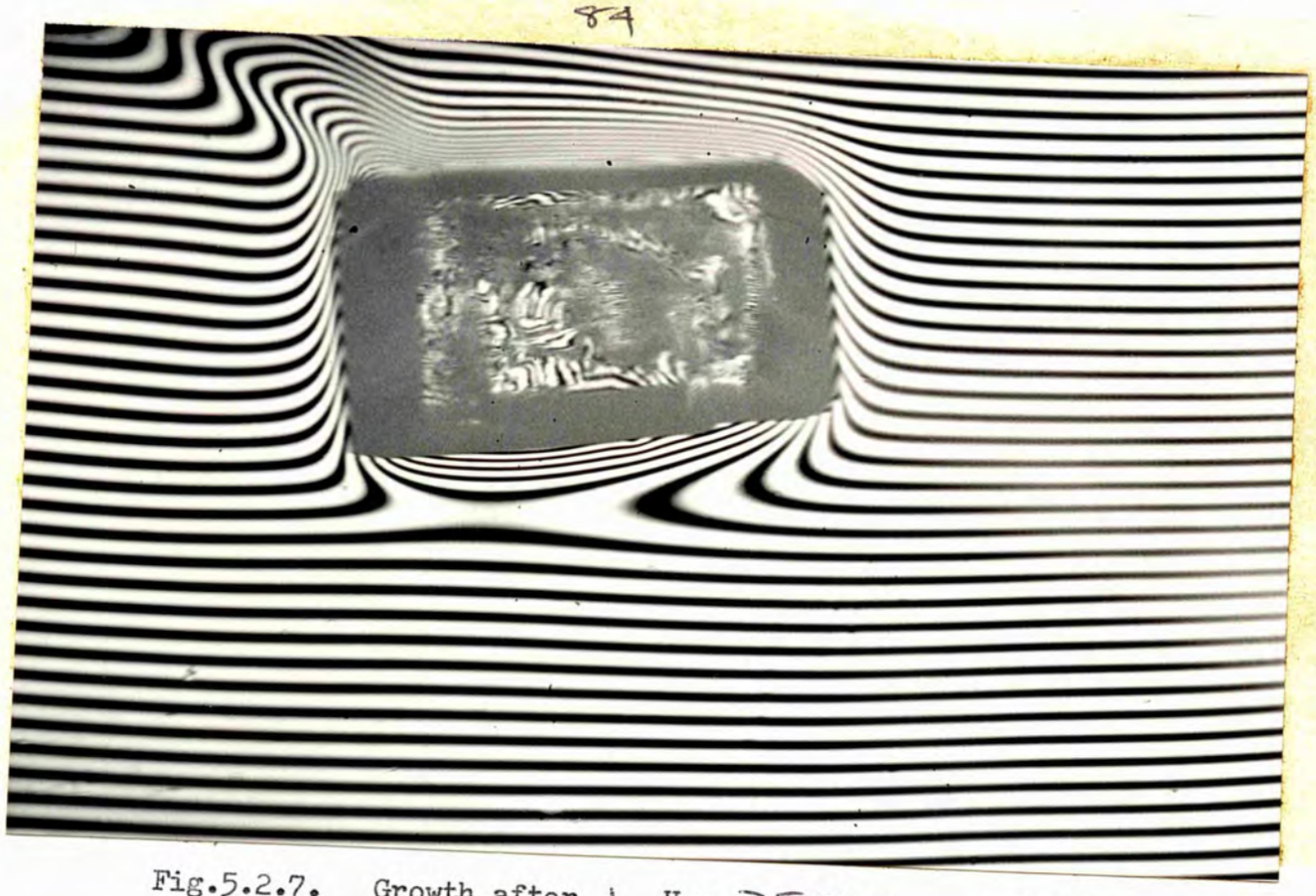


Fig.5.2.7. Growth after 1 Hrs. 35 Mins. x 17.5.

Fig. 5.2.8. Growth after 6 Hrs. 35 Mins. x 17.5.

Crystal 2.

The initial concentration of the solution was 75.7%.

The stages of growth of this crystal are shown in Figs. 5.2.1 - 5.2.8. The streaming effect was established almost immediately. This was generally observed when solutions of greater concentration were used.

One detail to be observed, which is of interest, is in the fringes when they reach the edges of the crystal AD and BC. It can be seen that the fringes suddenly turn back sharply producing a slight 'hook' effect. This was at first thought to be an out of focus effect but on certain photographs it can be seen quite distinctly in the solution, e.g. along edge BC in Fig . 5.2.6. It can also be observed in certain photographs of the previous series e.g. DA in Fig. 5.1.4. It was only ever seen along the edges of the natural crystal when they were in this position. A possible explanation is that the concentration of the solution around the crystal decreases and then as the edge is approached there is a sudden rather sharp increase. From measurements made it would mean that this layer of increased concentration would be approximately 0.03 mm. in thickness, and this is of greater depth than any layer ever predicted to exist round a growing crystal. It is difficult to draw any further conclusions when it is remembered that this effect occurs along

an edge where two faces meet and not along an actual face of the crystal.

Initially the streaming again originates some distance along the upper face of the crystal and during growth moves along towards corner A, and as it does so it changes from initially being perpendicular to the face until in the final picture Fig. 5.2.8. it is inclined at approximately 35° to the vertical. The concentration of the solution at the centre of the streams remains constant at a value of 74.95% until 22 mins. after the start of the experiment it has fallen to 74.85% and this value is maintained for the rest of the observed growth period.

The concentration along the edges also remains approximately constant throughout the period of growth (always being within 1% of the value of the initial concentration of the solution). The value near the centre of the lower edge being 75.45% and 75.6% at each of the corners C and D. At the centres of BC and DA the value is lower, being 75.3% and falls still further to 75.2% at the corners A and B along these edges.

The fringes in the bulk of the solution are remarkably straight and parallel everywhere, being only disturbed in a small region round the crystal due to the convection effects.

Table 5.2. shows the variation of concentration with the change in fringe order.

TABLE 5.2.

t = 0.172 cms.
μ = 1.4792
λ° = 5461 Å

Δn	$\Delta \mu$	Refractive index at the edge μ.	Concentration at the edge.
1	0.0003	1.4789	75.6%
1.5	0.0005	1.4787	75.5%
2	0.0006	1.4786	75.45%
2.5	0.0008	1.4784	75.4%
3	0.0010	1.4782	75.3%
4	0.0013	1.4779	75.2%
5	0.0016	1.4776	75.1%
6	0.0019	1.4773	74.95%
7	0.0022	1.4770	74.85%

Fig. 5.3.1. Growth after — Hrs. 26 Mins. x 18

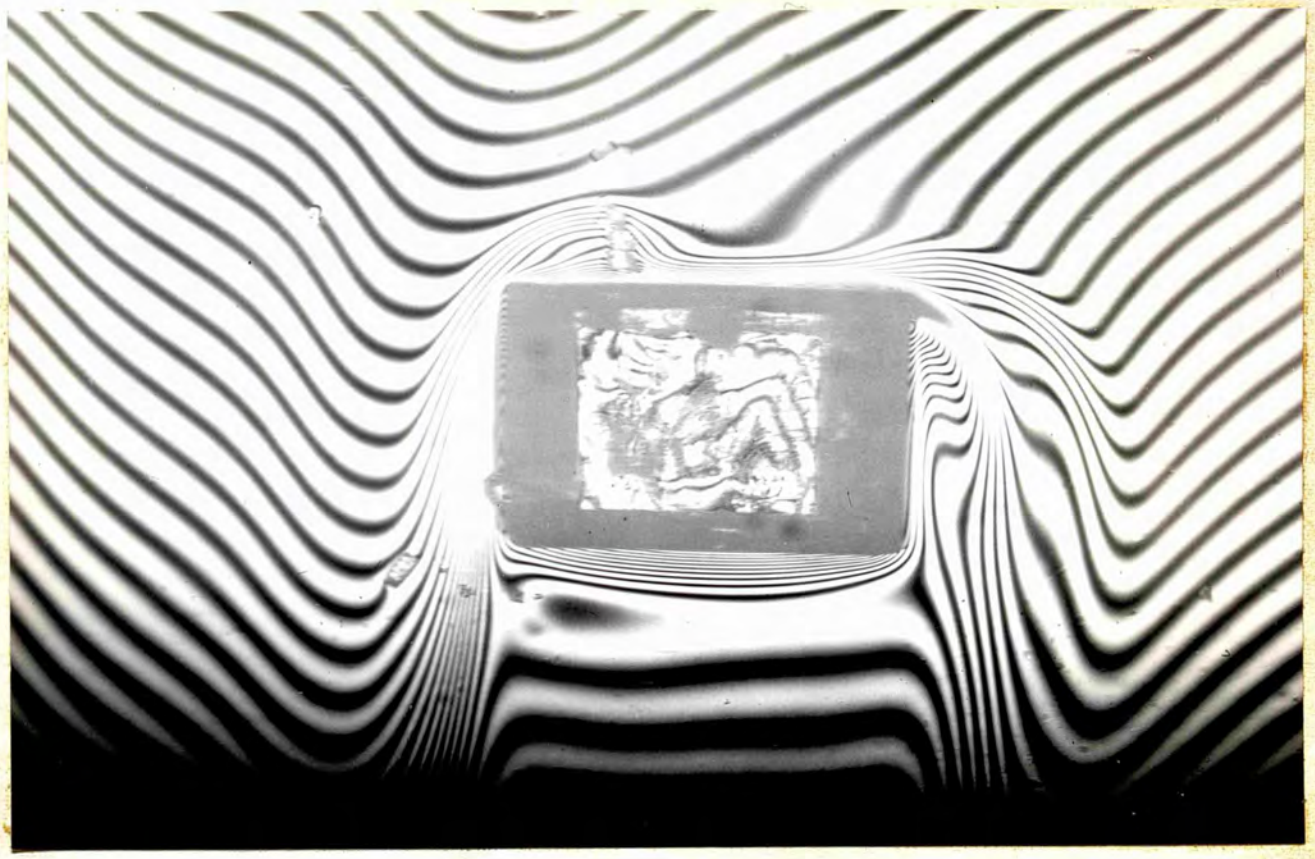


Fig. 5.3.2. Growth after (Hrs. — Mins. x 18

Fig. 5.3.3. Growth after 1 Hrs. 30 Mins. x 18

Fig. 5.3.4. Growth after 2 Hrs. 8 Mins. x 18

Fig. 5.3.5. Growth after 2 Hrs. 32 Mins. x 18

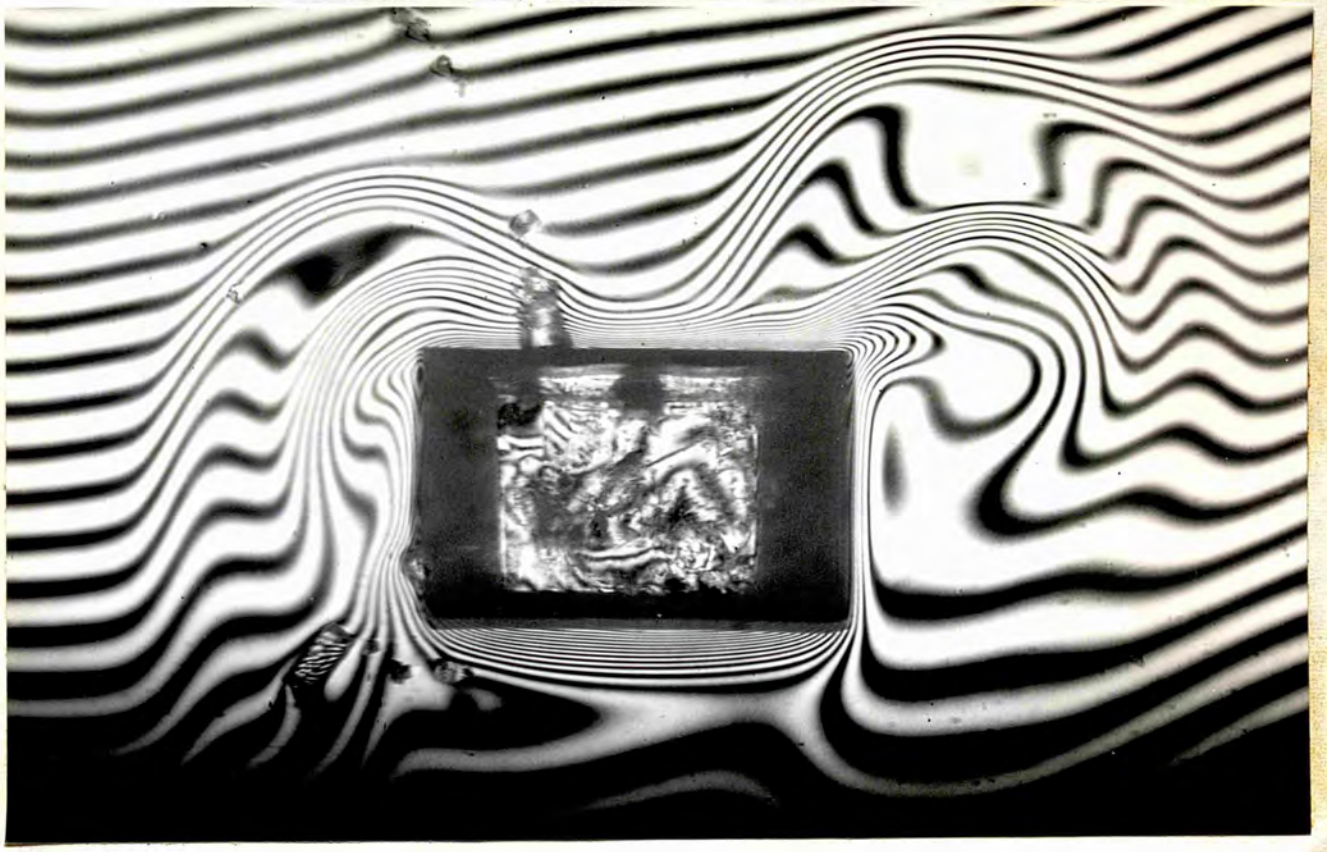


Fig. 5.3.6. Growth after 3 Hrs. 2 Mins. x 18

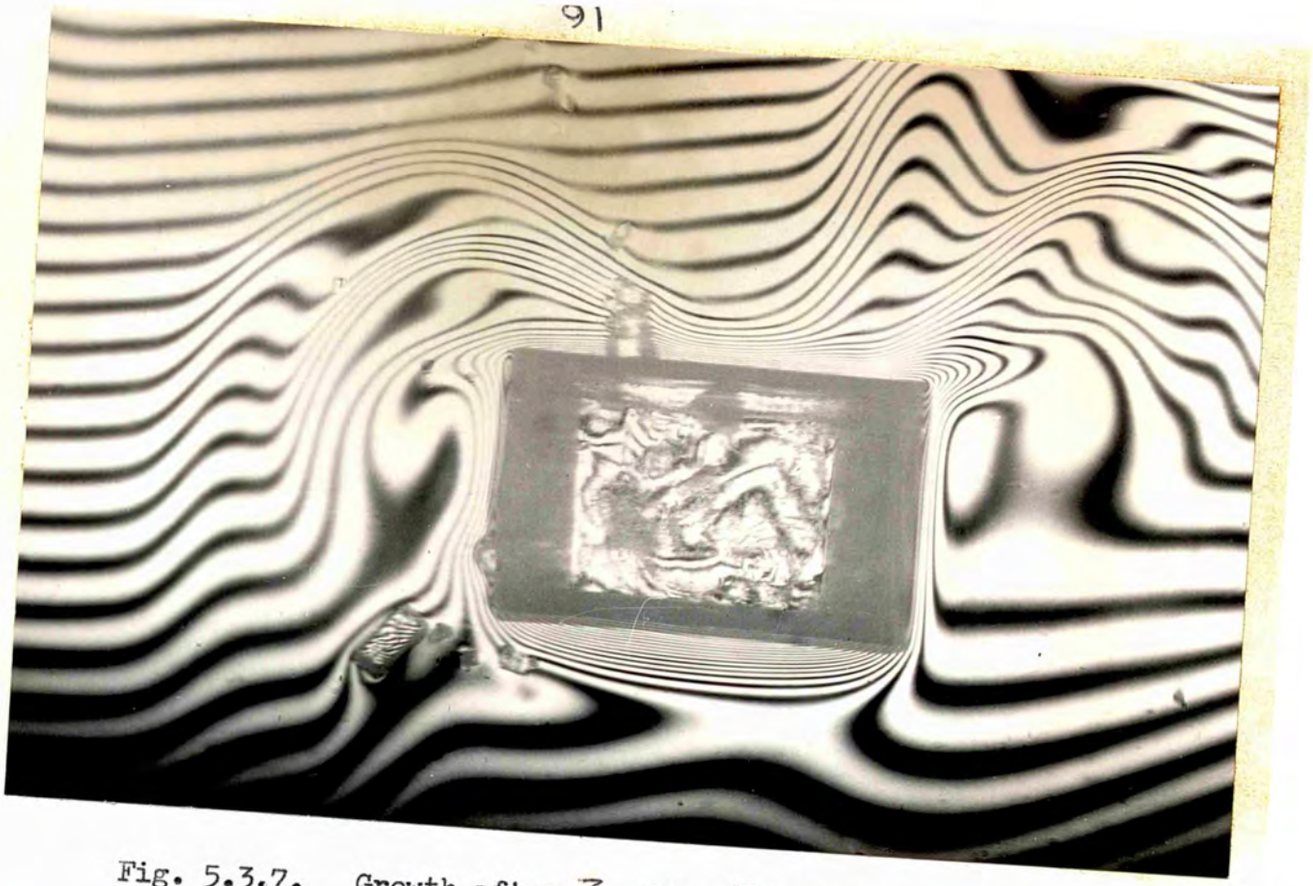


Fig. 5.3.7. Growth after 3 Hrs. 31 Mins. x 18

Fig. 5.3.8. Growth after 4 Hrs. — Mins. x 18

Fig. 5.3.9. Growth after 4 Hrs. 40 Mins. x 18

Crystal 3.

This crystal, as in the case of the previous one, was grown in a solution of 75.7% concentration. The results are remarkably different.

Unfortunately the fringe field is much too disturbed to permit any calculation but the effects due to convection are well illustrated.

In Fig. 5.3.1. 26 mins. after the start the effect of the down streaming due to dissolution can still be seen. At a time of 1 hour there are indications at the corner B that a 'lobe' is trying to develop and there is also an upward movement in the solution at corner A.

This upward flow is further accentuated in Fig. 5.3.3. and is breaking up into distinct separate 'streams', the 'lobe' at the corner B being further developed. In Fig. 5.3.6. there appears to be a 'lobe' developing also at corner A, and this is later confirmed. These highly disturbed conditions continued throughout the period of 4½ hours that growth was observed and the distinct streaming from the upper face generally observed with crystals growing in such a concentrated solution was never completed.

One effect that is noticeable is the building up of the concentration gradient along the face CD as the process of growth

continues. In Fig. 5.3.9 this is quite remarkable, normally such steep gradients were not observed with the natural crystal in this position.

Presumably this is in evidence because the depleted solution is not being removed as no streaming is established. When the experiment was started small nuclei were seen to originate along the face AB and at the corner D these have grown to quite an extent especially the one near the bottom left hand corner. Perhaps it is due to the presence of these crystals that the normal "streamline flow" is being prevented and the observed 'turbulent' conditions result.

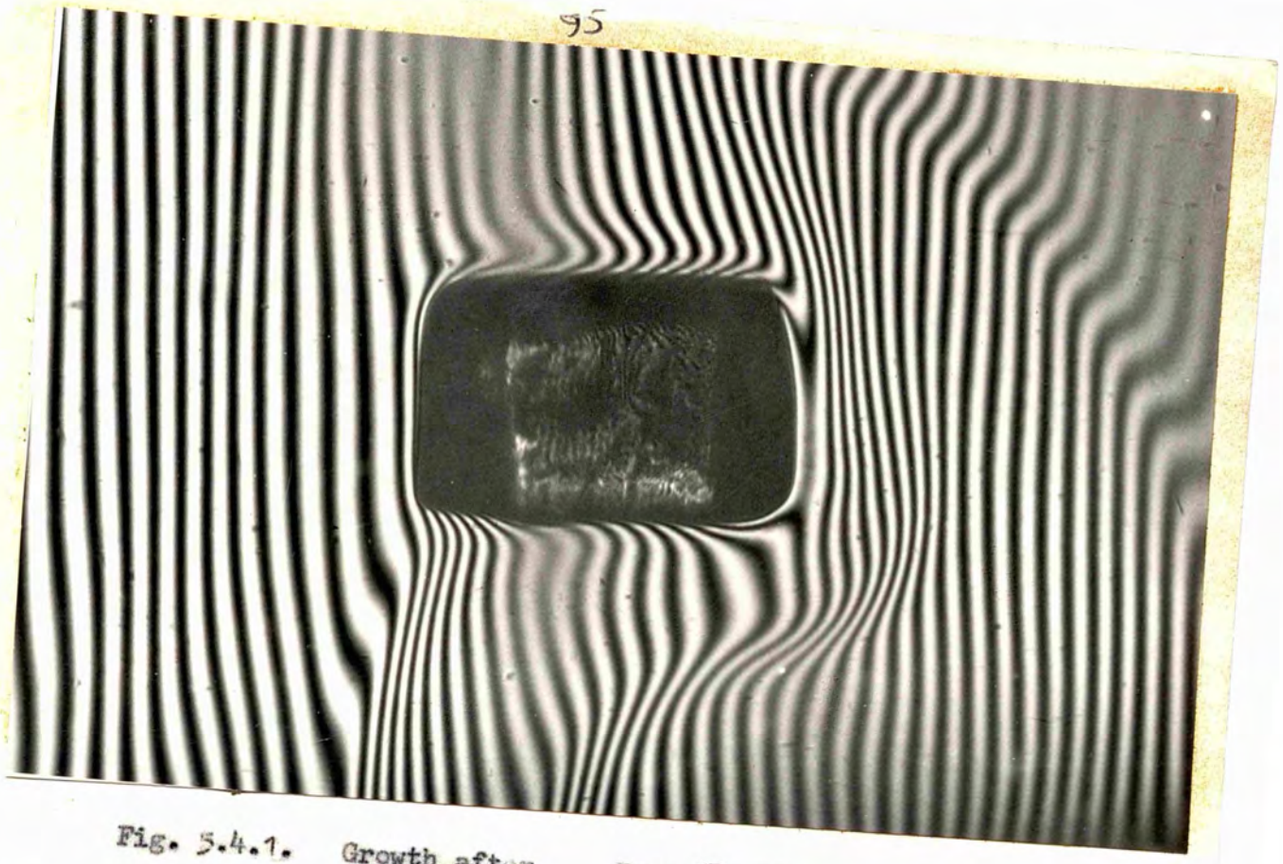


Fig. 5.4.1. Growth after Hrs. 13 Mins. x 19

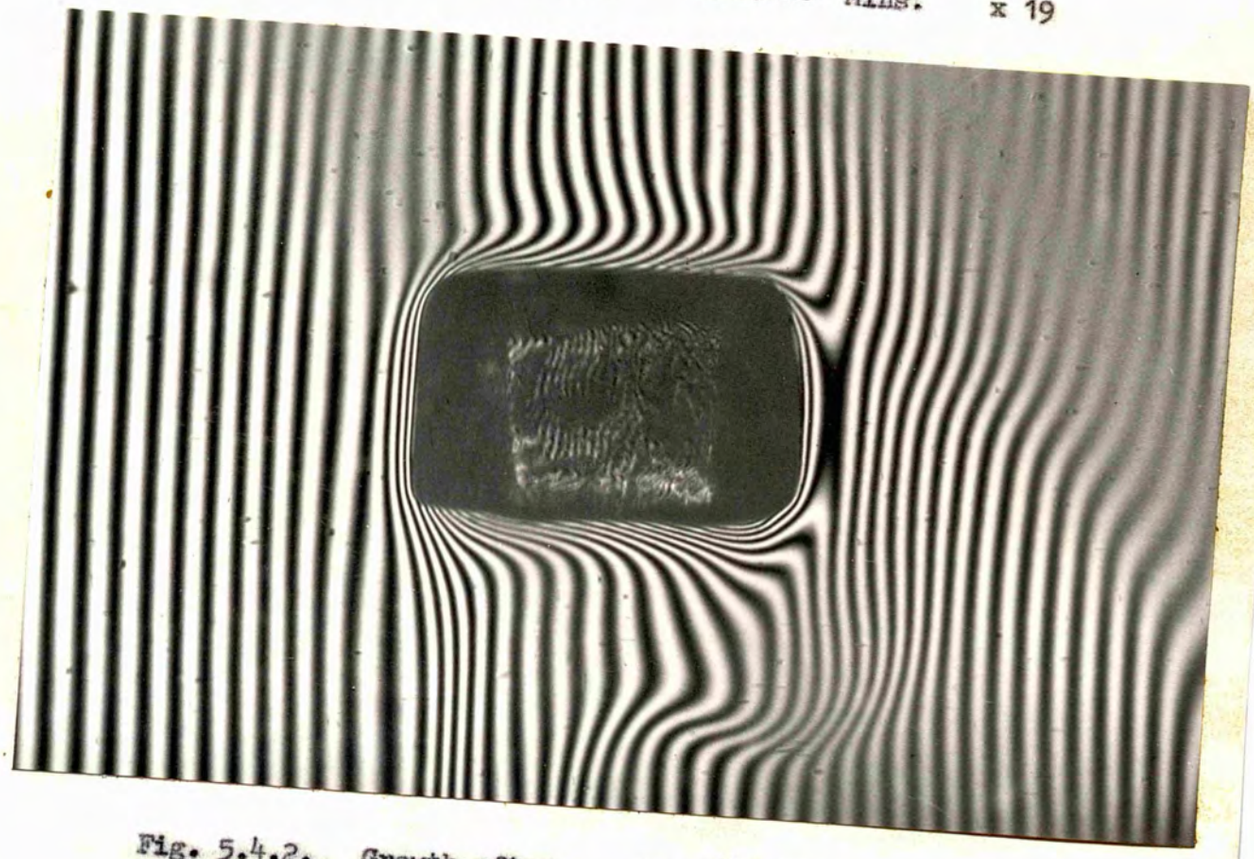


Fig. 5.4.2. Growth after Hrs. 17 Mins. x 19

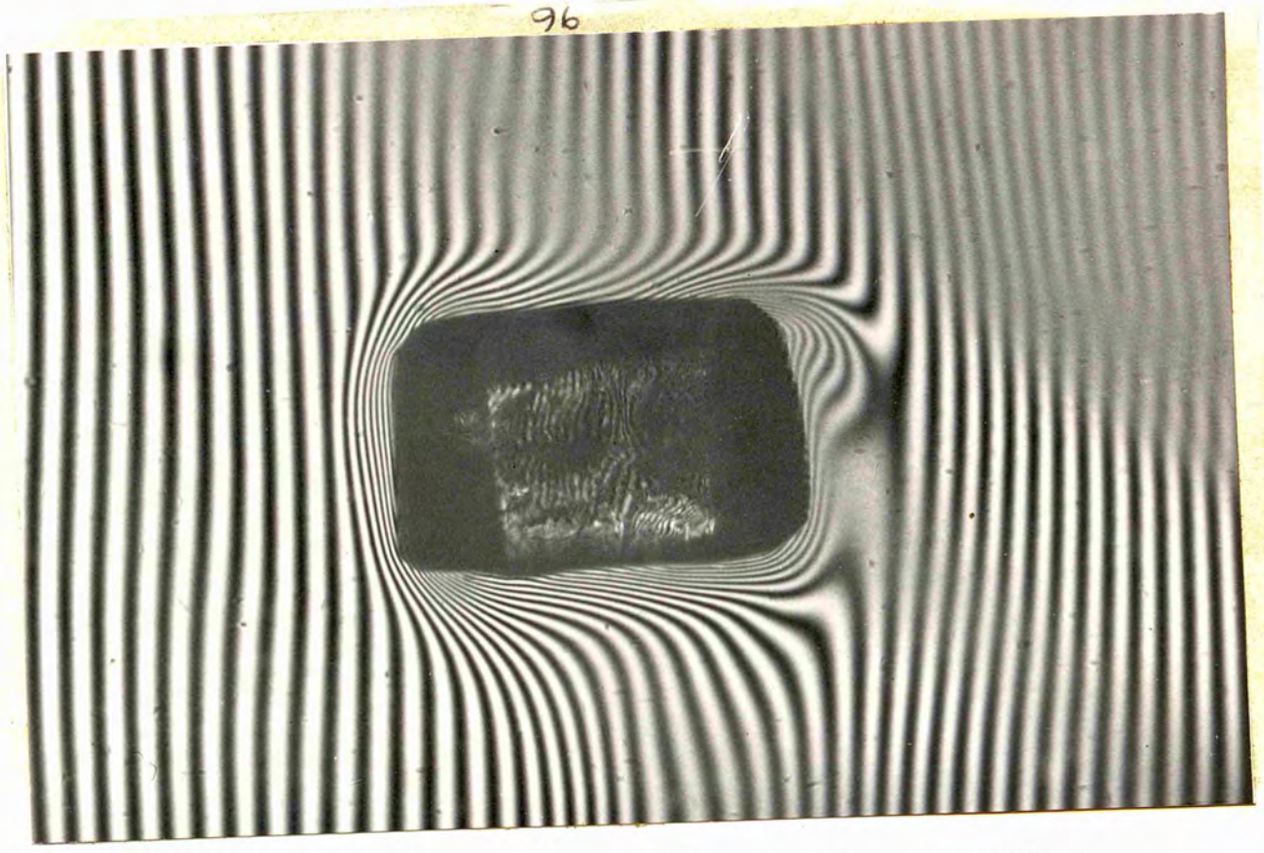


Fig. 5.4.3. Growth after Hrs. 26 Mins. x 19

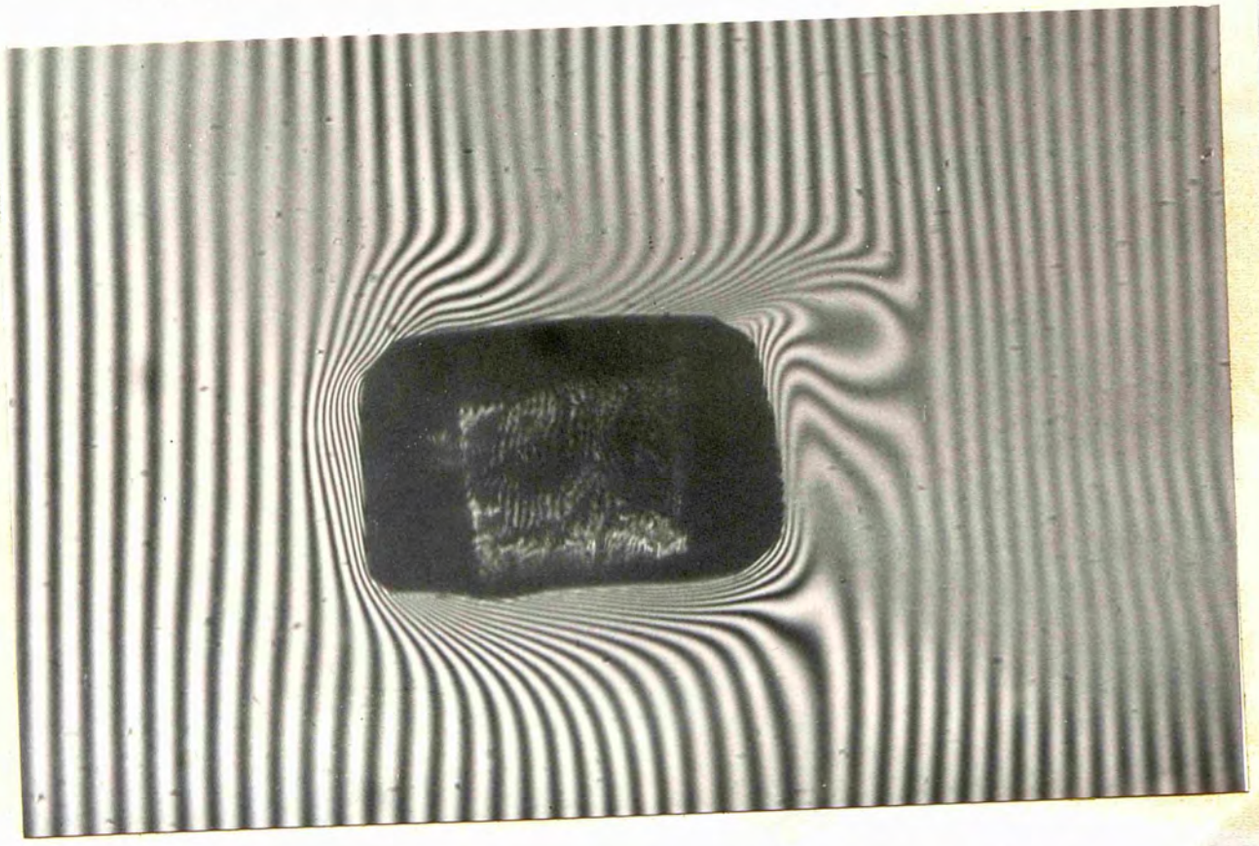


Fig. 5.4.4. Grwoth after Hrs. 34 Mins. x 19

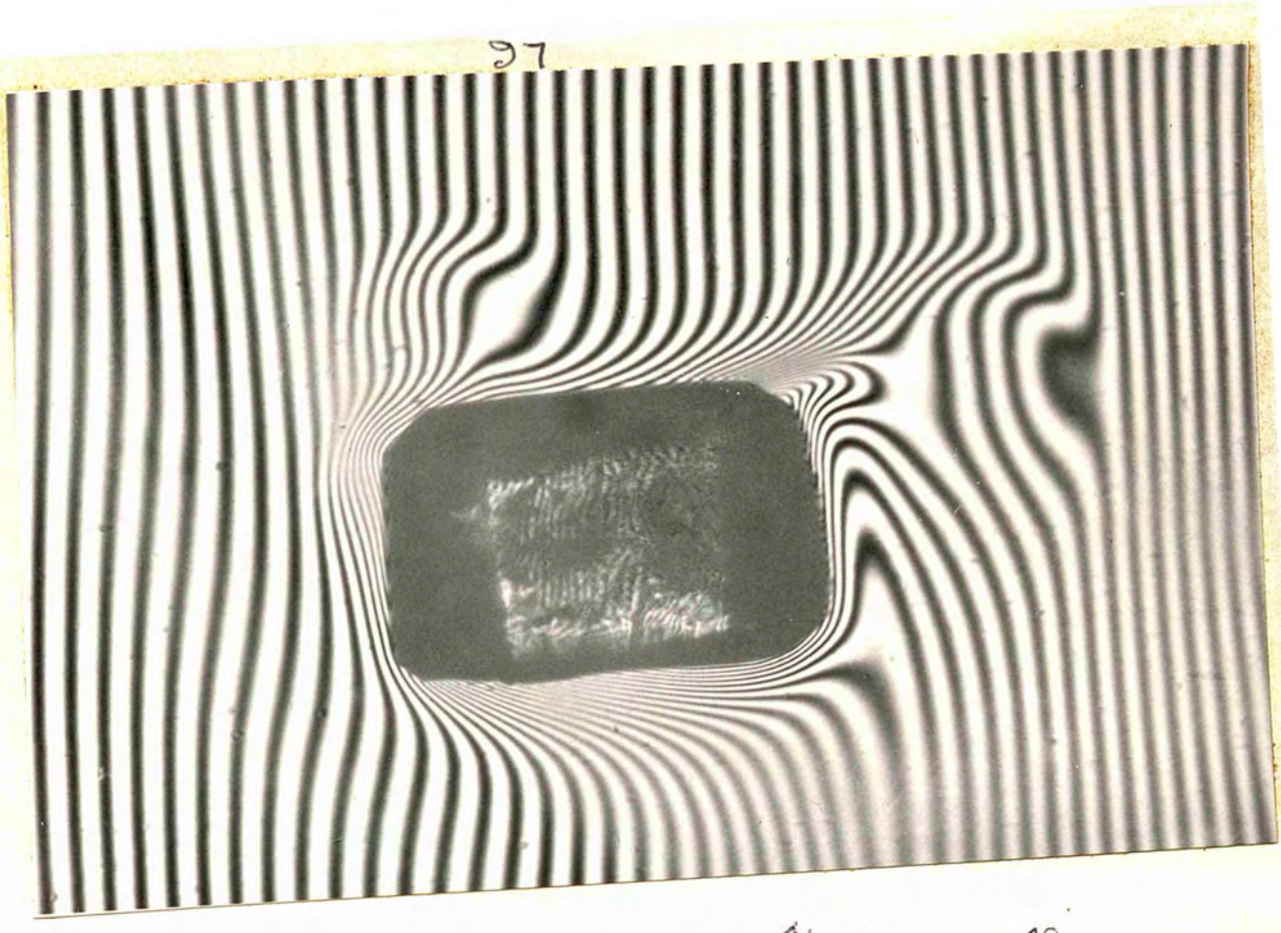


Fig. 5.4.5. Growth after Hrs. 41 Mins. x 19

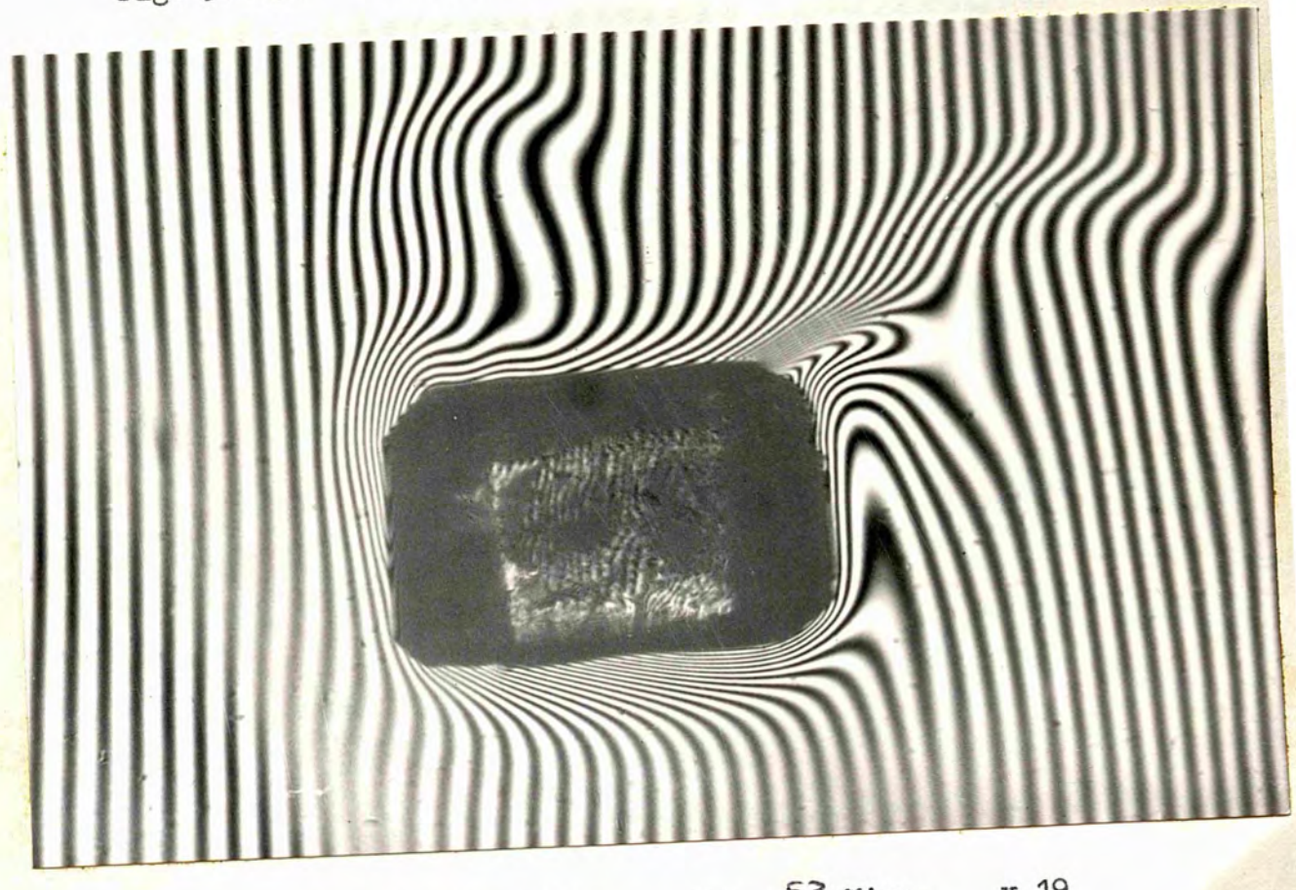


Fig. 5.4.6. Growth after Hrs. 53 Mins. x 19

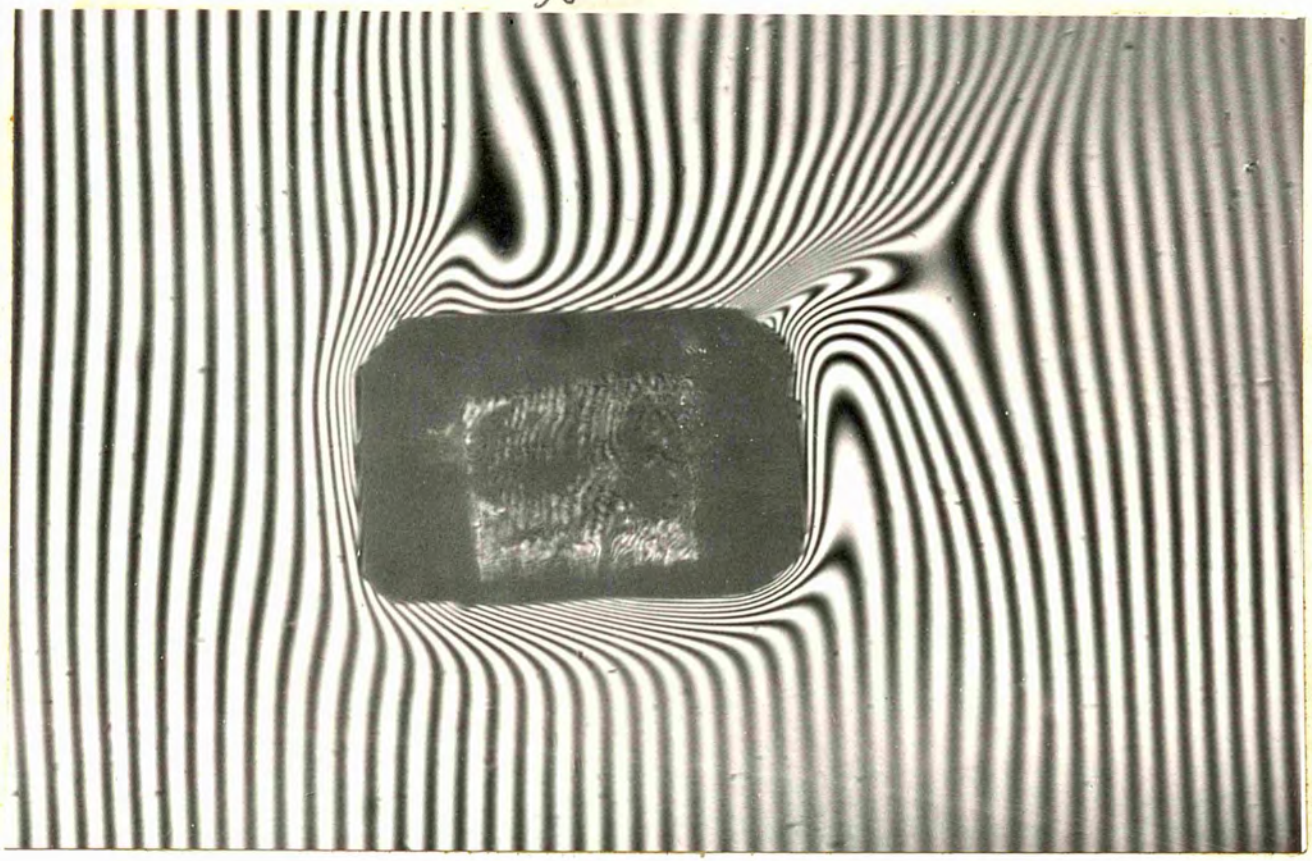


Fig. 5.4.7. Growth after 1 Hrs. 8 Mins. x 19

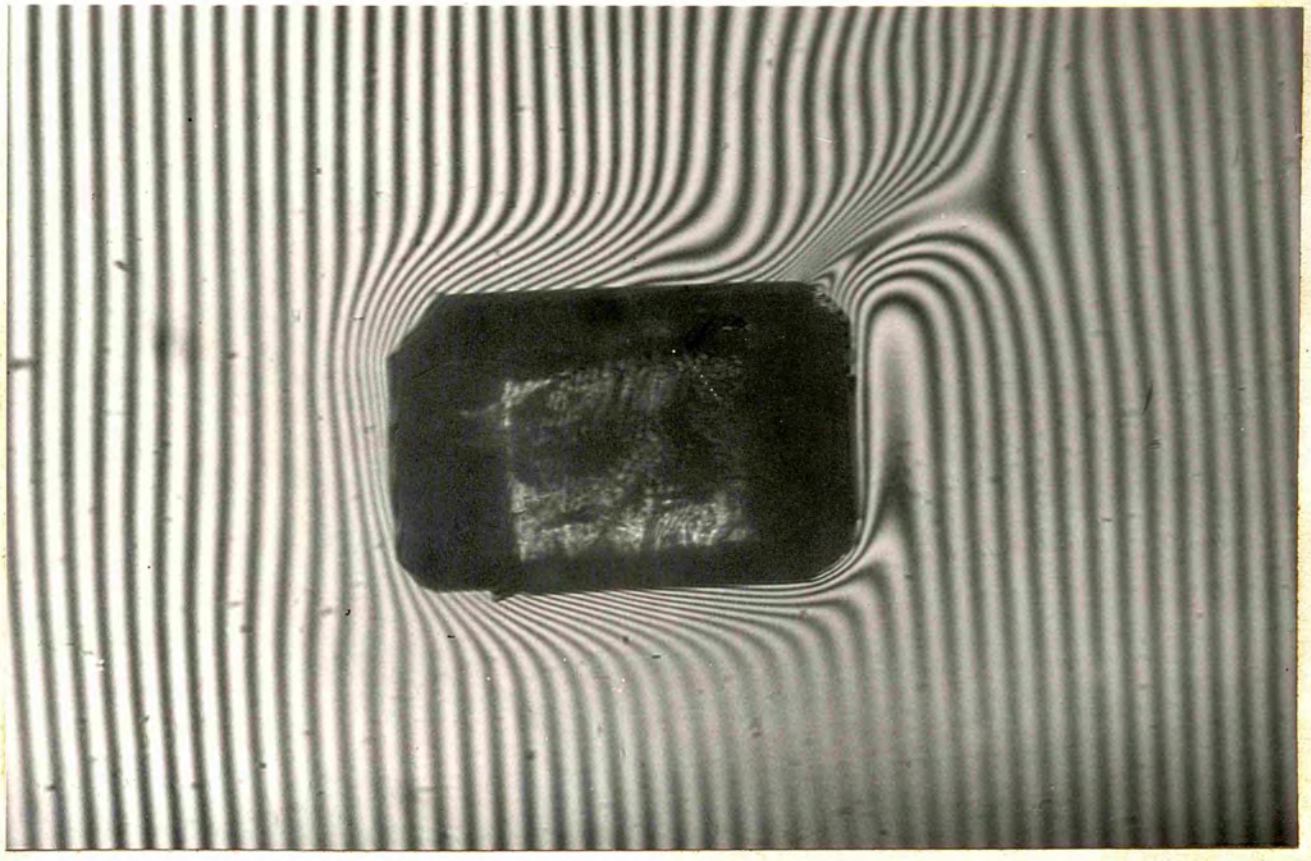


Fig. 5.4.8. Growth after 1 Hrs. 41 Mins. x 19

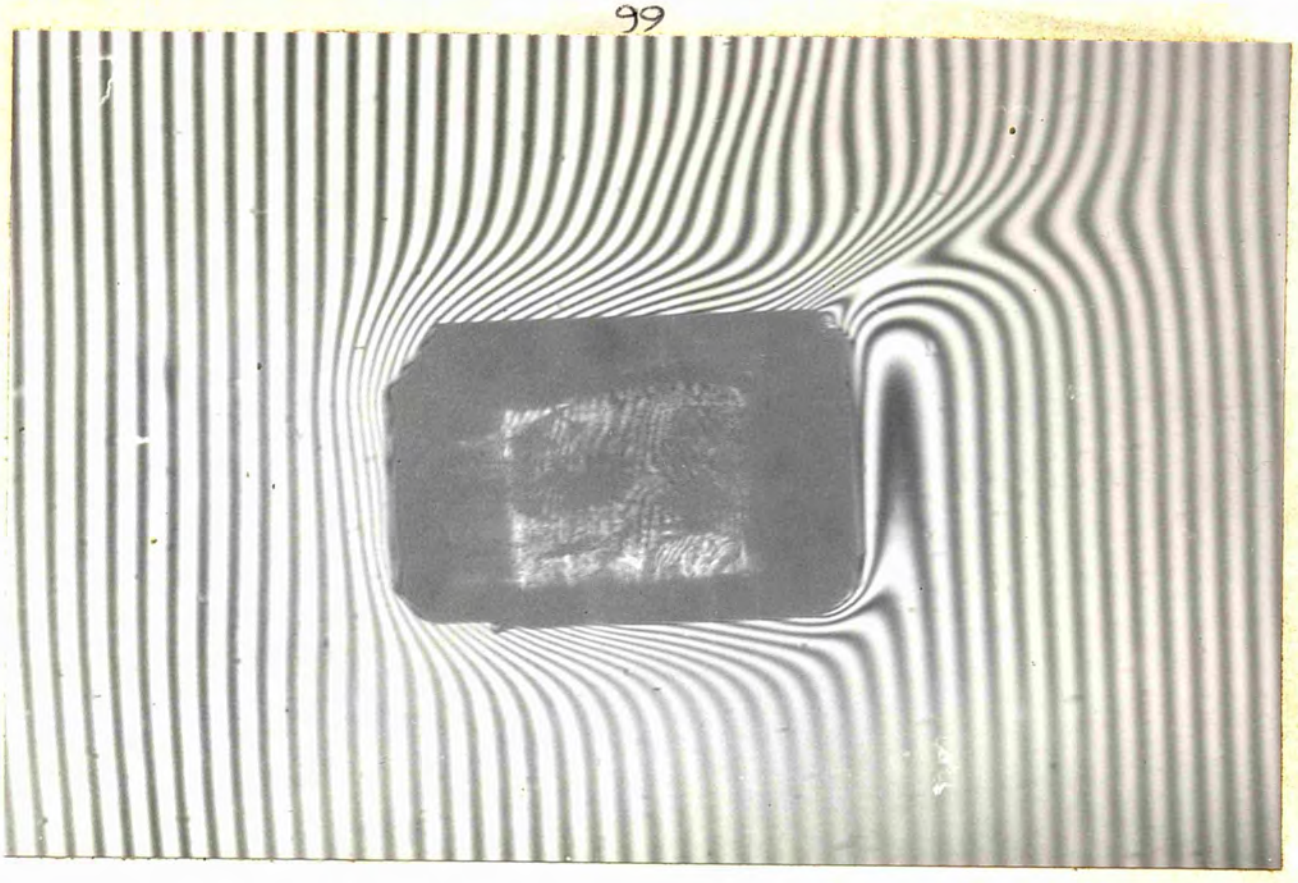


Fig. 5.4.9. Growth after 1 Hrs. 48 Mins. x 19

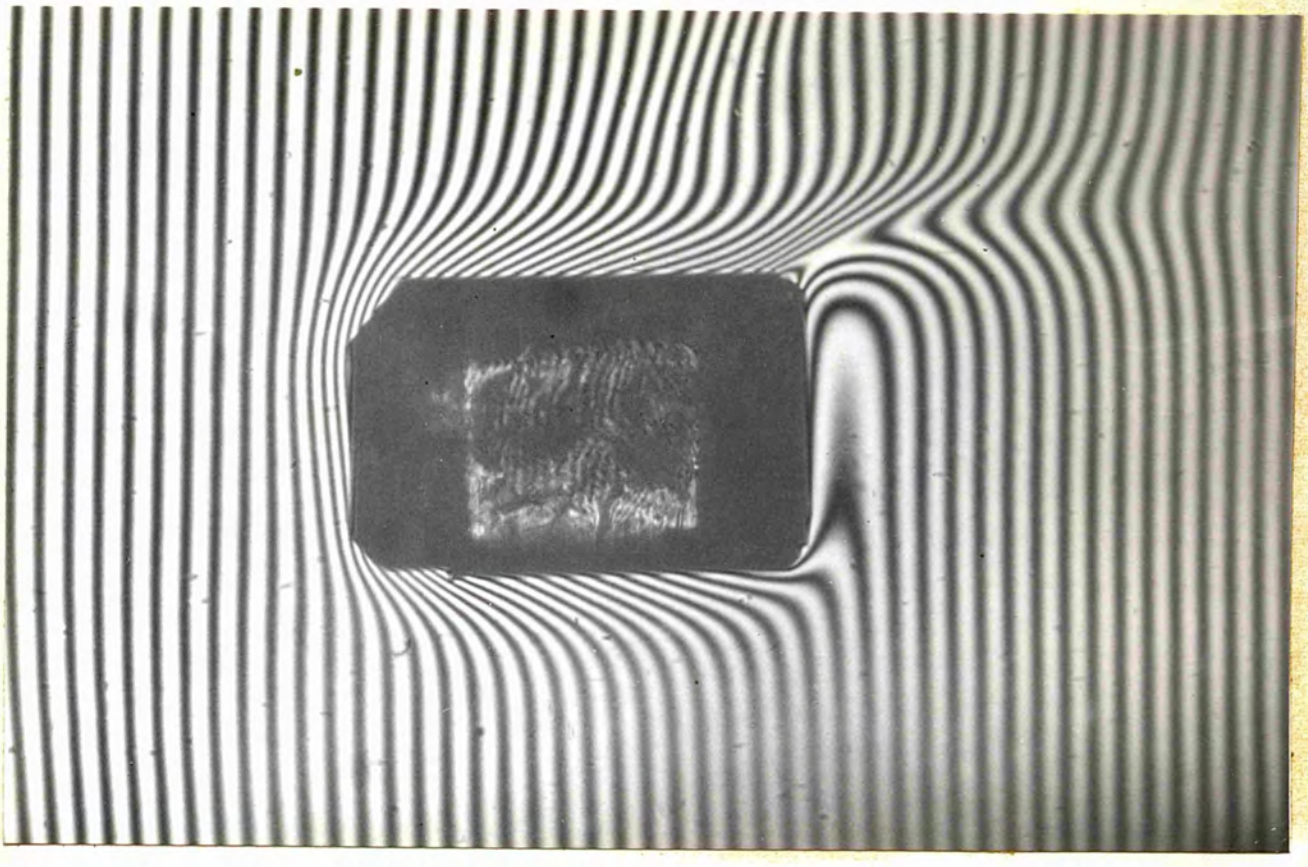


Fig. 5.4.10. Growth after 2 Hrs. 47 Mins. x 19

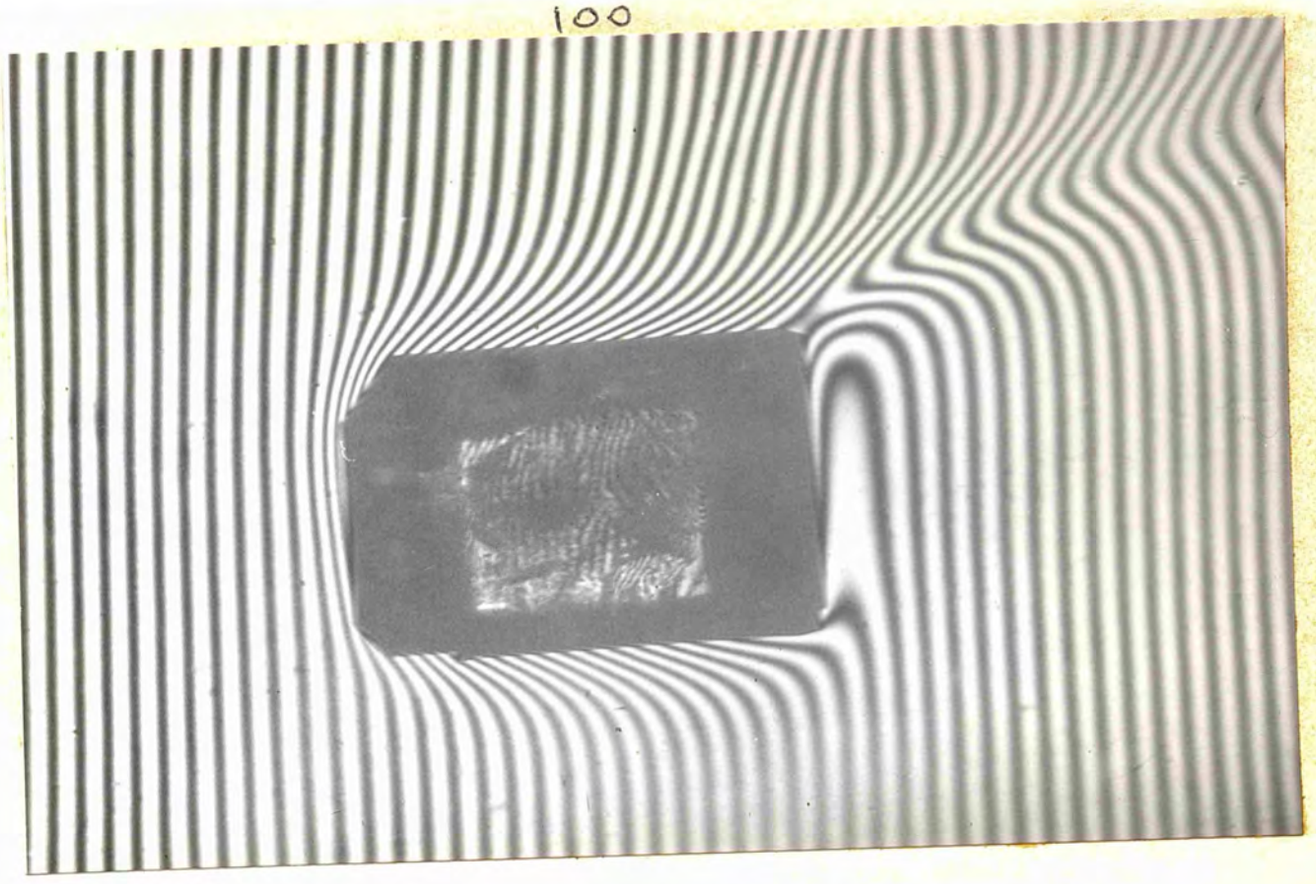


Fig. 5.4.11. Growth after 3 Hrs. 57 Mins. x 19

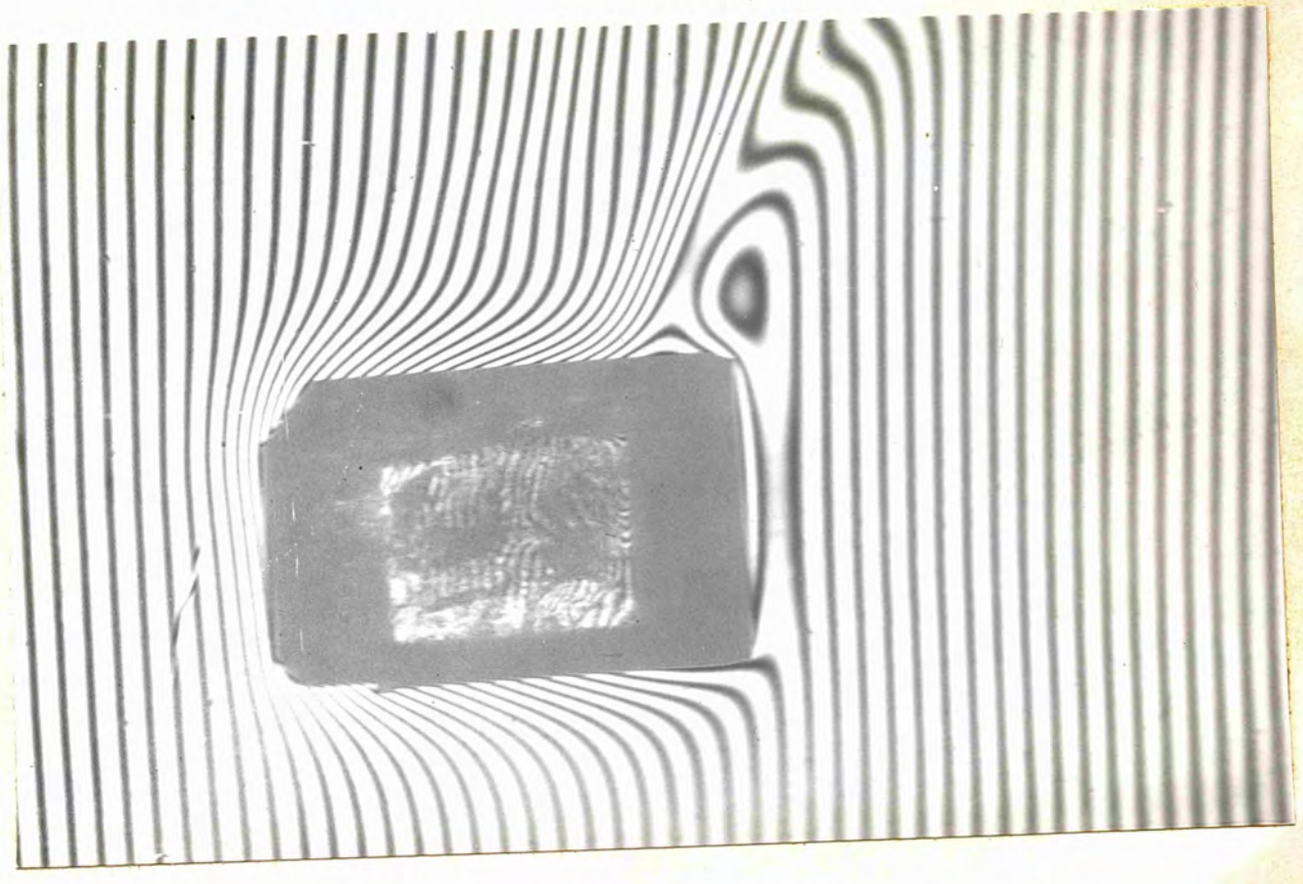


Fig. 5.4.12. Growth after 5 Hrs. 38 Mins. x 19

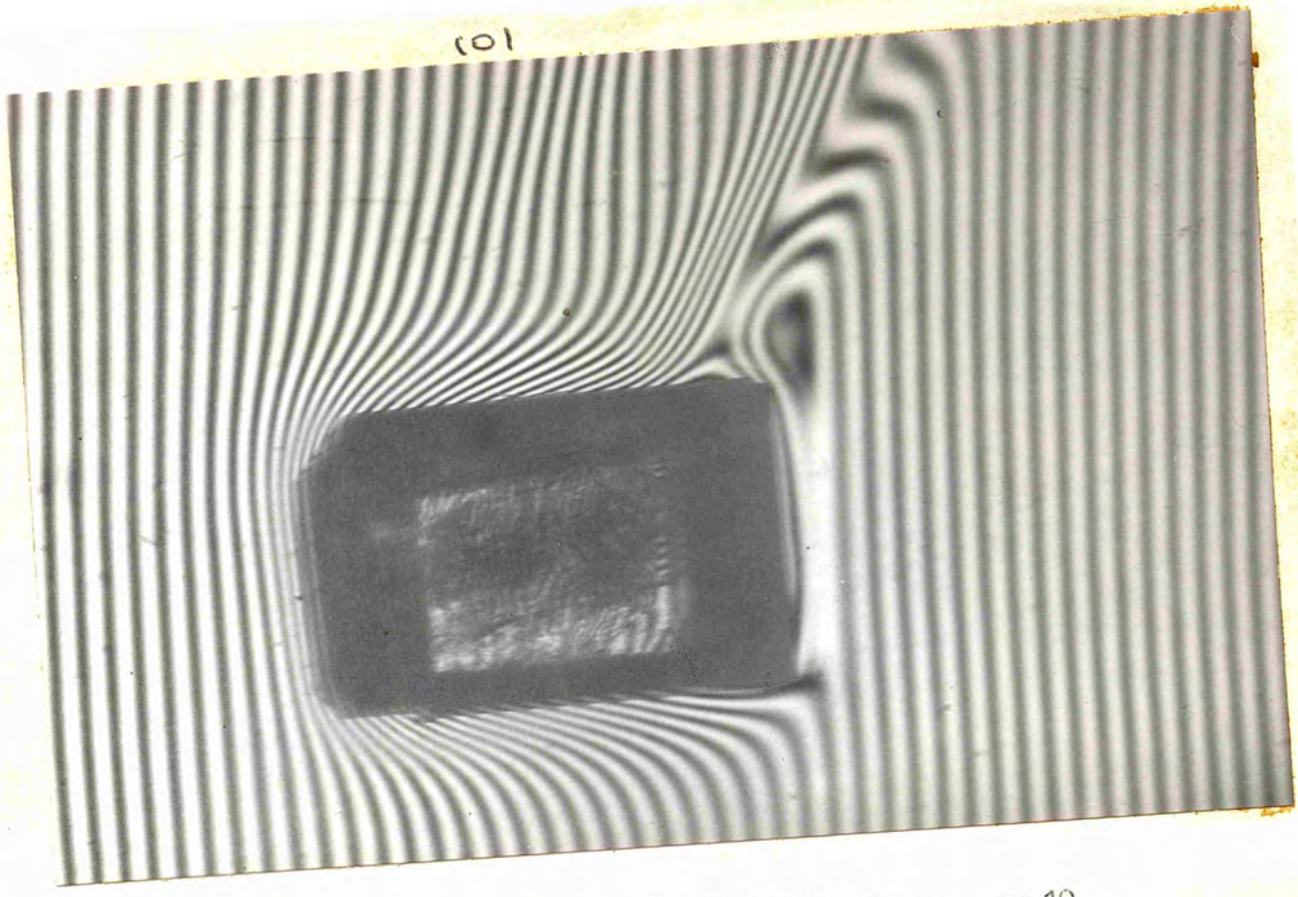


Fig. 5.4.13. Growth after 6 Hrs. 52 Mins. x 19

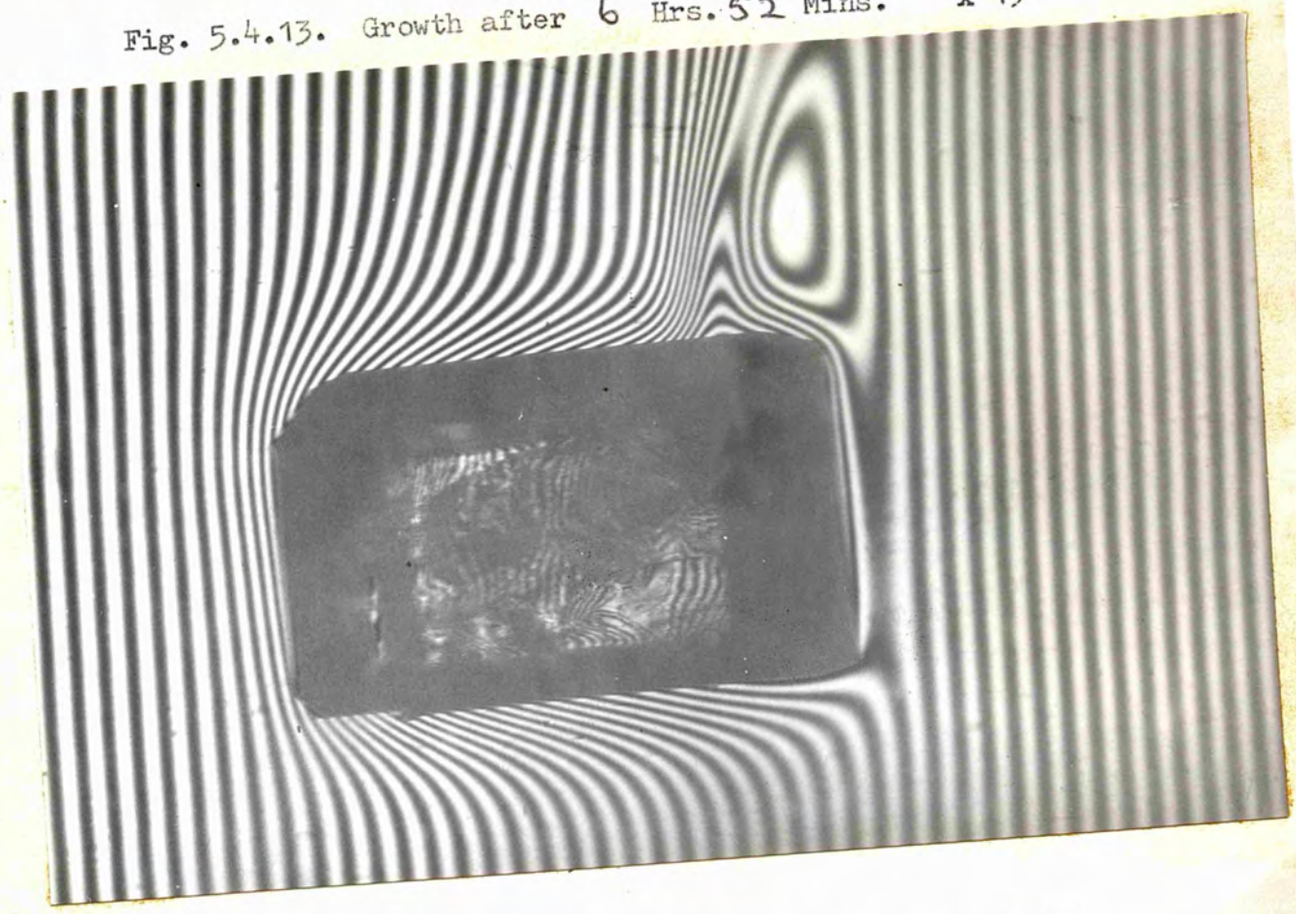


Fig. 5.4.14. Growth after 19 Hrs. Mins. x 19

Crystal 4

The initial concentration of the solution was 71.6%

In this experiment the plates of the interferometer are oriented so that the fringes are vertical.

On the right of the crystal the deviated fringes are widely spaced whereas on the left they are close together. The reason is, that, on the right, the gradient of refractive index is directed away from the crystal i.e. against the direction of increasing wedge height; the gradient thus opposes the increase in optical path and leads to wide fringe spacing. On the left the gradient enhances the increase in optical path and therefore narrows the fringe spacing.

In the first photograph the disturbance in the lower half is again due to dissolution. This can still be seen 4 mins. later but during this time the gradients round the crystal have built up, and the concentration at the lower face, for instance, has fallen rapidly from a value of approximately 71.4% to 70.85%. The chart in Fig. 5.4.15 illustrates graphically how the concentration at the faces was calculated throughout this work, whenever possible. The numbers indicate the change in fringe order at the positions indicated by the arrows. From table 5.4. the corresponding concentration at the face can be found.

At a time of 26 mins. the characteristic 'lobe' can be seen developing at the right hand edge. There are indications at the left hand edge, in Figs. 5.4.4. and 5.4.5 , of a similar development but this does not materialize. Meanwhile the streaming from corner B is becoming established and during the time the concentration at the lower edge is falling until it reaches its minimum value of 69.9% at a time of 53 mins. The streaming would appear fully in operation at a time of 1 hour 8 mins. when the concentration at the lower face has risen to a value of 70.2%. showing that the depleted solution has been removed and replaced by fresh material.

The angle of inclination of the stream again changes during the process of growth initially it is at an angle of approximately 45°. to the vertical and in the final photograph it has become almost vertical.

The chart Fig. 5.4.15, illustrates how the concentration along the various edges changes during growth. This again shows how the value of the concentration falls until the process of convection becomes established when it increases and then remains approximately constant. The concentration at the lower corners C is a maximum for the conditions at any particular time. That at the corner D varies.

Initially it can be seen that faces of the form $\{0\ 1\ 1\}$ occur on both sides of the crystal. Those on the left hand side

become more definite as the crystal grows while those on the right are eliminated. This is in accordance with the fact the sucrose crystal belongs to the sphenoidal class of the monoclinic system and therefore shows this lateral asymmetry.

The conditions in the solution at D reflect on these happenings. The concentration although greater than at the centre of the face is much less than at the corner C falling to a minimum value of 70.3%. at a time of 1 hour 8 mins. (when the concentration along the edge CD is at its minimum value). After this streaming becomes established and this face begins to grow out and eliminate iteself, the concentration at the face having increased.

The concentration along the lower edge CD has decreased in the final stages of the experiment although along BC and DA it has been maintained at a value of 71.25%

This concludes the report on the growth of natural sucrose crystals. As stated previously the results obtained when the crystal is mounted in such a position complicate the analysis of the situation to a large extent. The investigation was therefore continued using ground crystals in the hope of simplifying the problem to a certain degree.

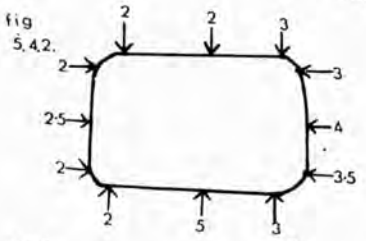
TABLE 5.4.

t = 0.162 cms.
μ_0 = 1.4689

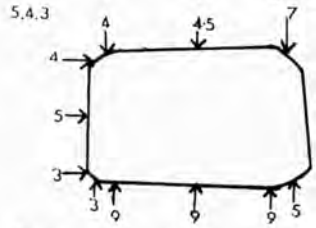
Δn	$\Delta \mu$	Refractive index at edge μ	Concentration at the edge.
1	0.0003	1.4686	71.4%
2	0.0007	1.4682	71.25%
3	0.0010	1.4679	71.15%
4	0.0013	1.4676	71%
5	0.0017	1.4672	70.85%
6	0.0020	1.4669	70.7%
7	0.0023	1.4666	70.6%
8	0.0026	1.4663	70.5%
9	0.0030	1.4659	70.3%
10	0.0034	1.4655	70.2%
11	0.0037	1.4652	70.05%
12	0.0040	1.4649	69.9%

FIG. 5.4.15

fig 5.4.2.



5.4.3



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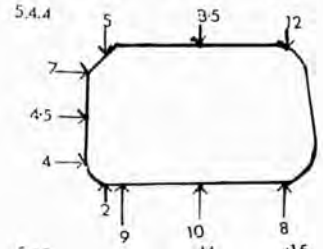

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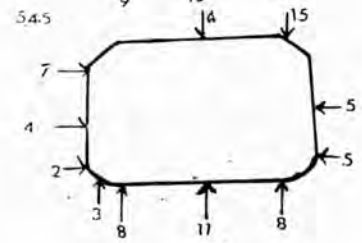

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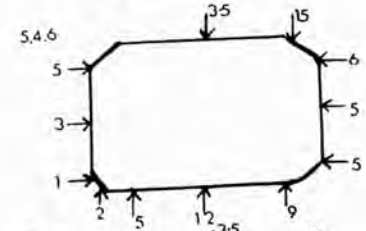

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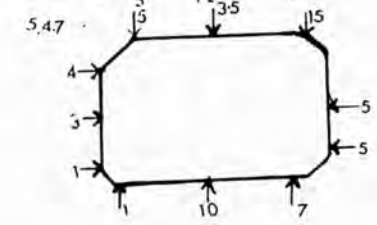

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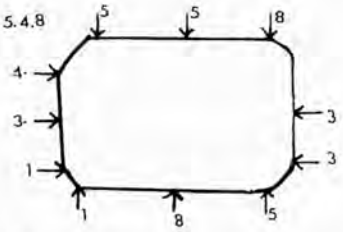

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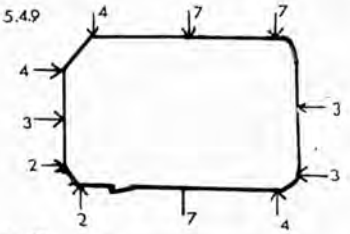

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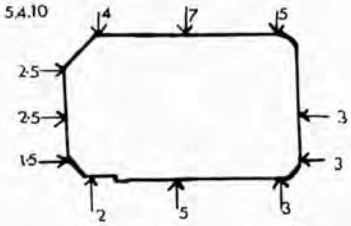

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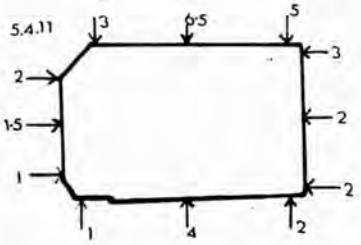

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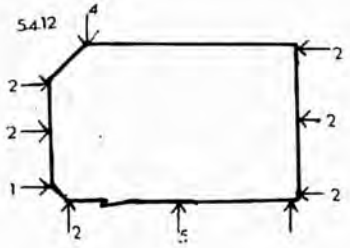

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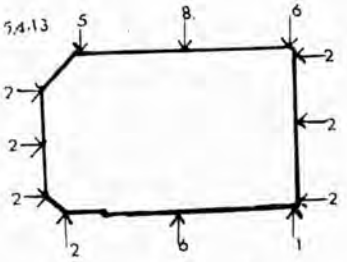
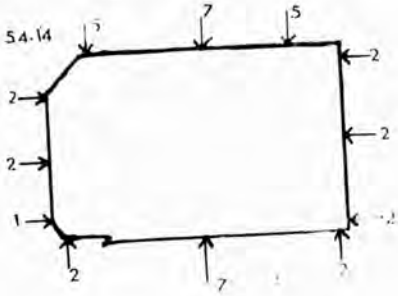


5.4.14



CHAPTER VI

GROWTH OF GROUND CRYSTALS

The determination of the concentration of the solution along a growing crystal face was not possible in the case of natural sucrose crystals. It was therefore decided to grind the crystal so that it could be mounted in such a way that fringes could be adjusted parallel or perpendicular to a face and the necessary information gained.

The crystals are labelled ABCDEF in a clockwise direction where A is the top left hand corner. On looking at Fig. 6.1.1. for example, ABCDEF is the ground face limited by the front wall of the cell nearest to the observer AB, BC, CD, DE, and EF are then the edges of the faces (1 0 0), (1 $\bar{1}$ 0) ($\bar{1}$ $\bar{1}$ 0) ($\bar{1}$ 0 0) ($\bar{1}$ 1 0), and (1 1 0) respectively which extend back into the picture in three dimensions. These are the faces on which growth is possible.

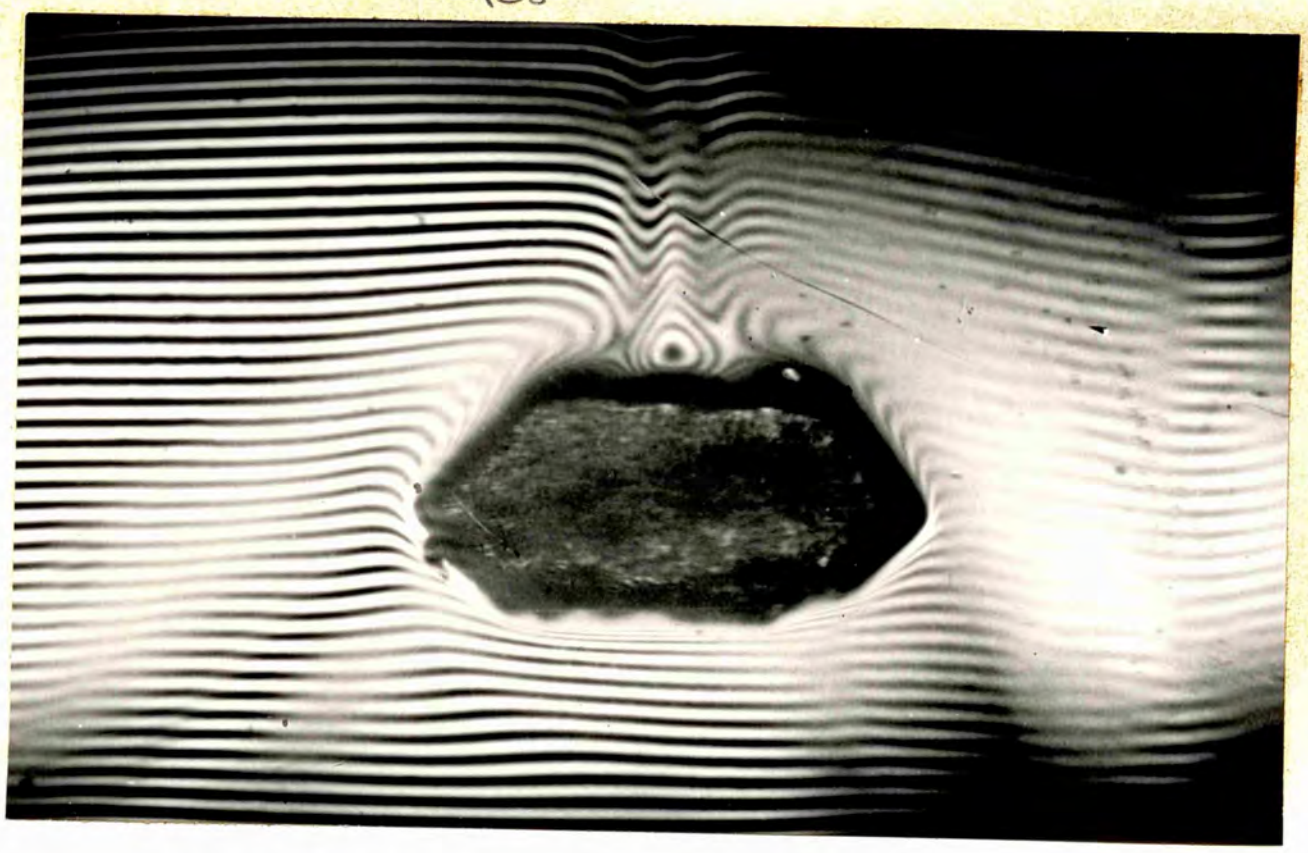


Fig. 6.1.1. Growth after Hrs. 4½ Mins. x 24

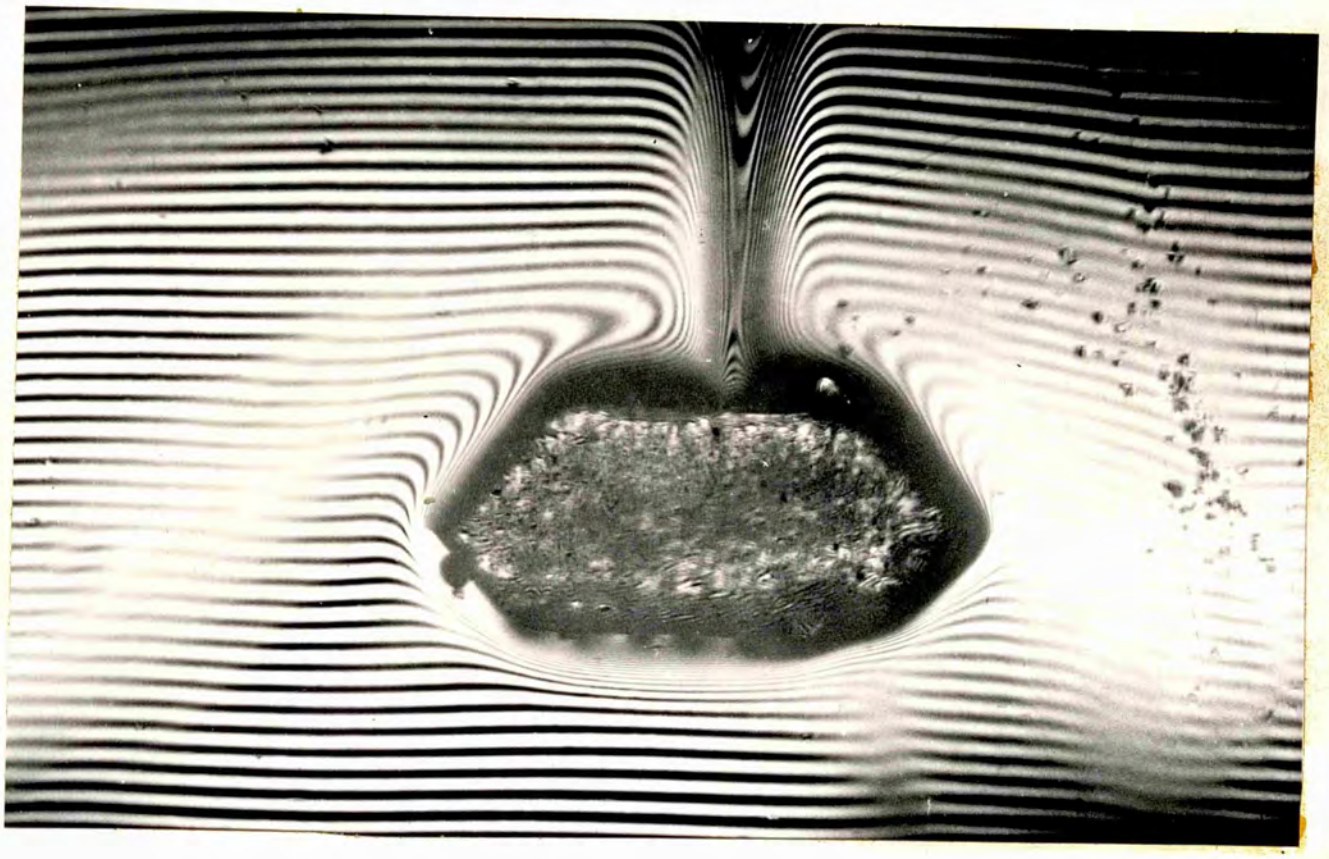


Fig. 6.1.2. Growth after Hrs. 22 Mins. x 24

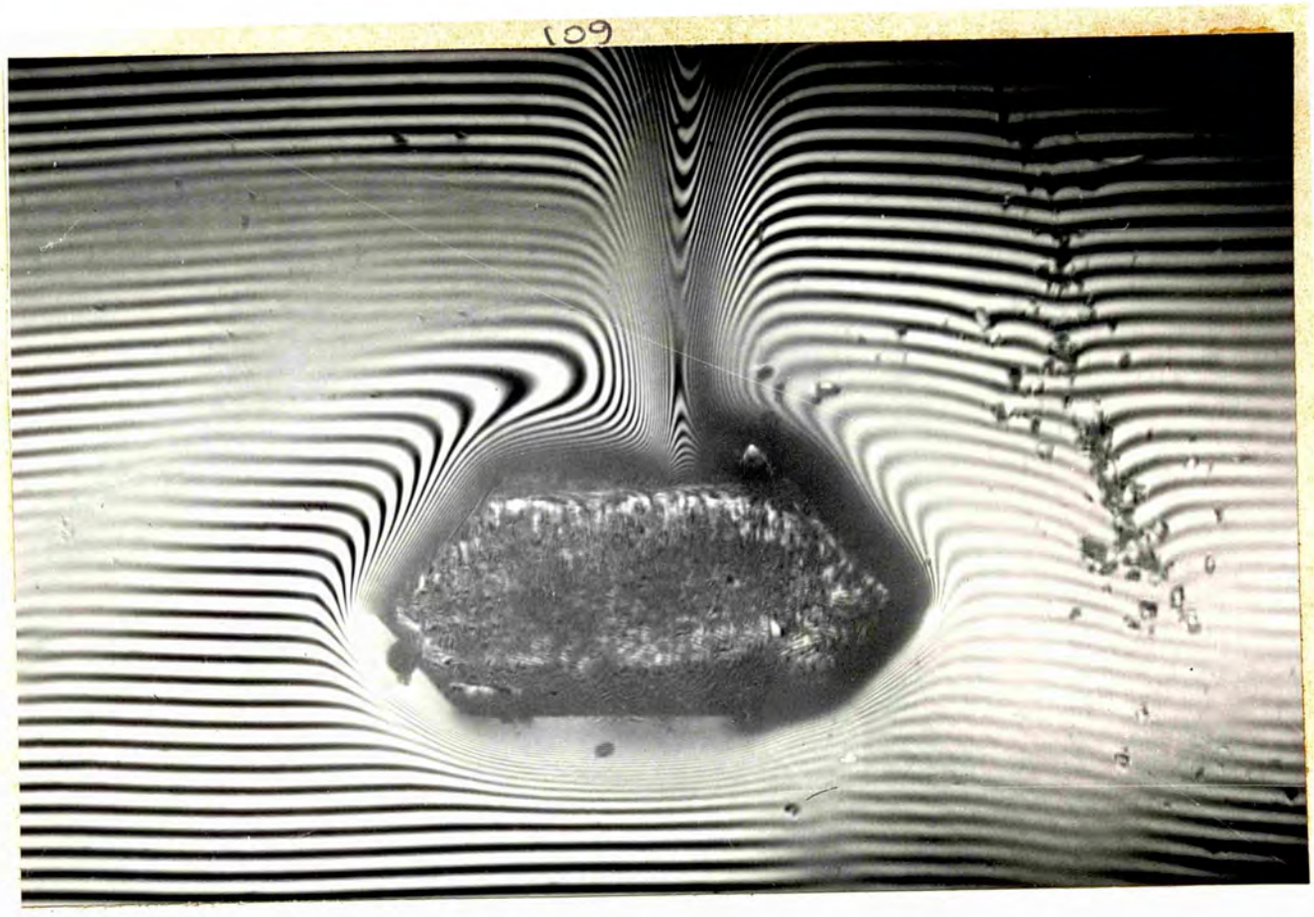


Fig. 6.1.3. Growth after 1 Hrs. 5 Mins. x 24

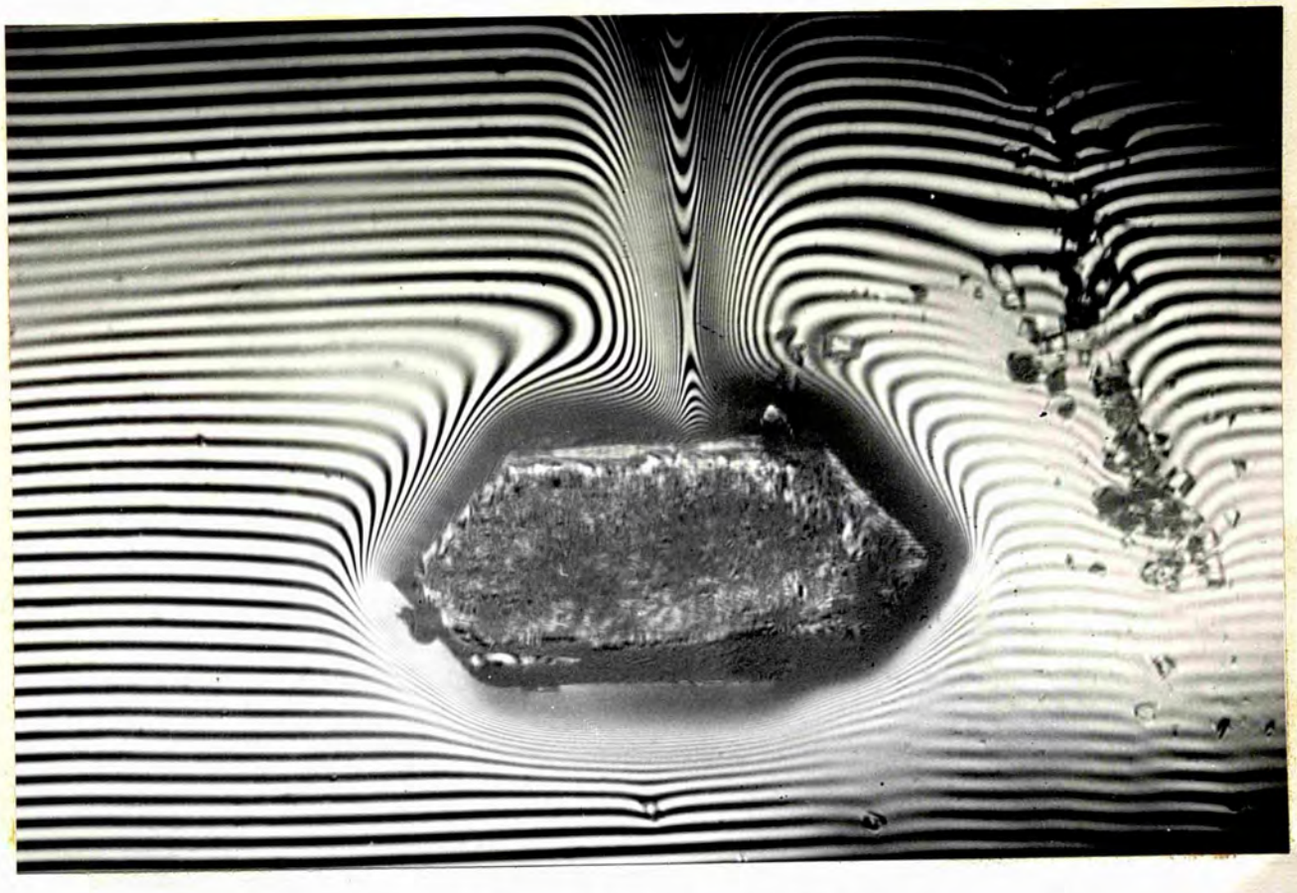


Fig. 6.1.4. Growth after 2 Hrs. 30 Mins. x 24

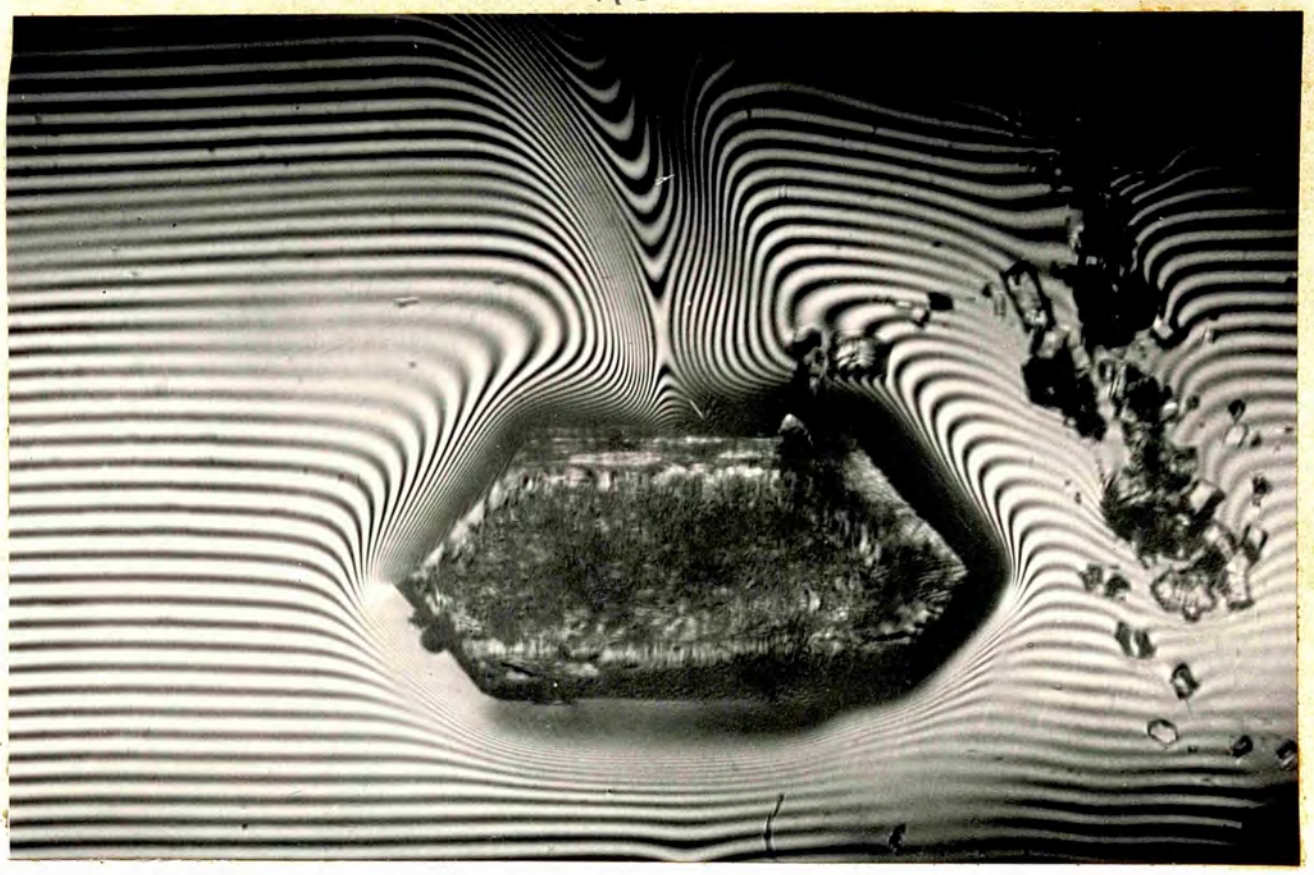


Fig. 6.1.5. Growth after 4 Hrs. 30 Mins. x 24

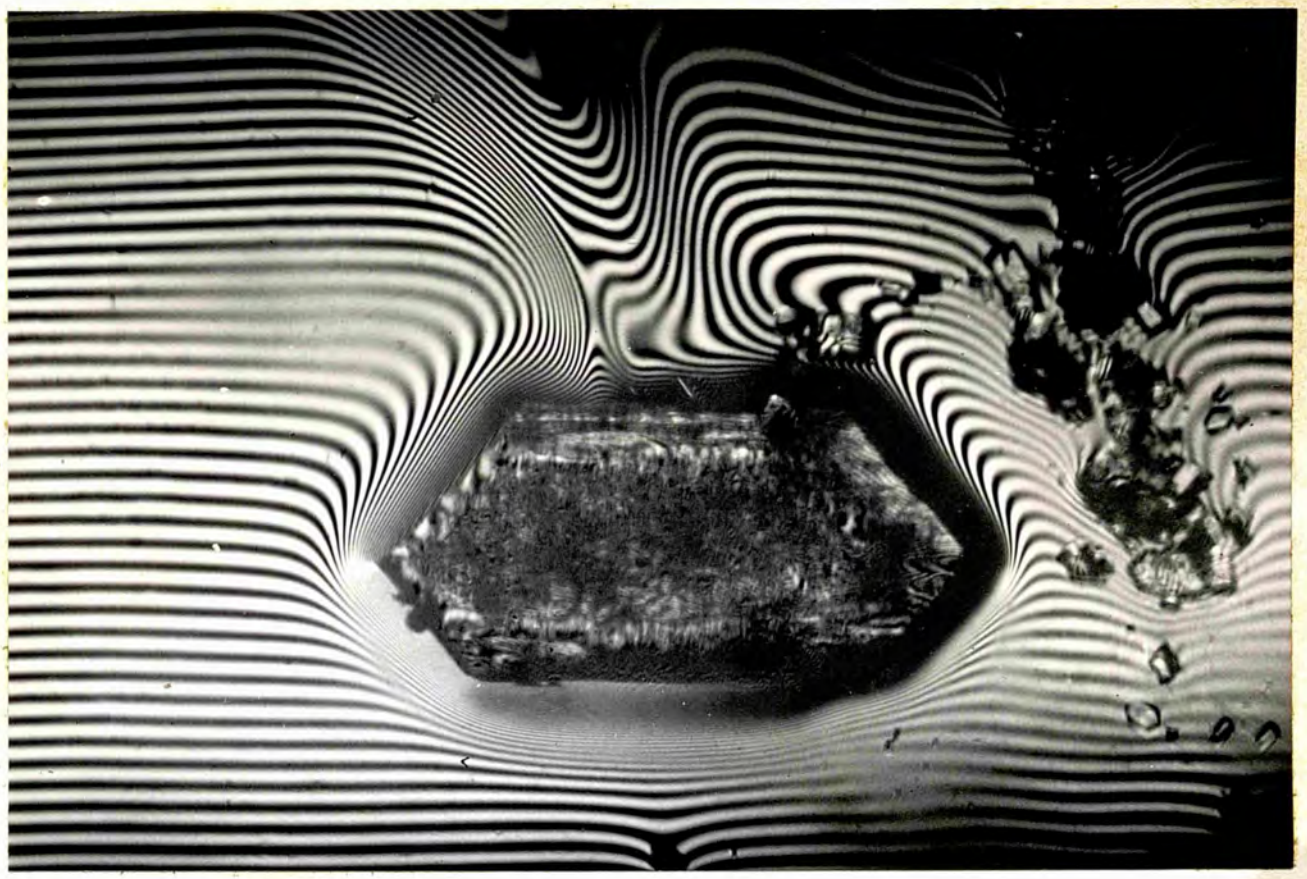


Fig. 6.1.6. Growth after 5 Hrs. 30 Mins. x 24

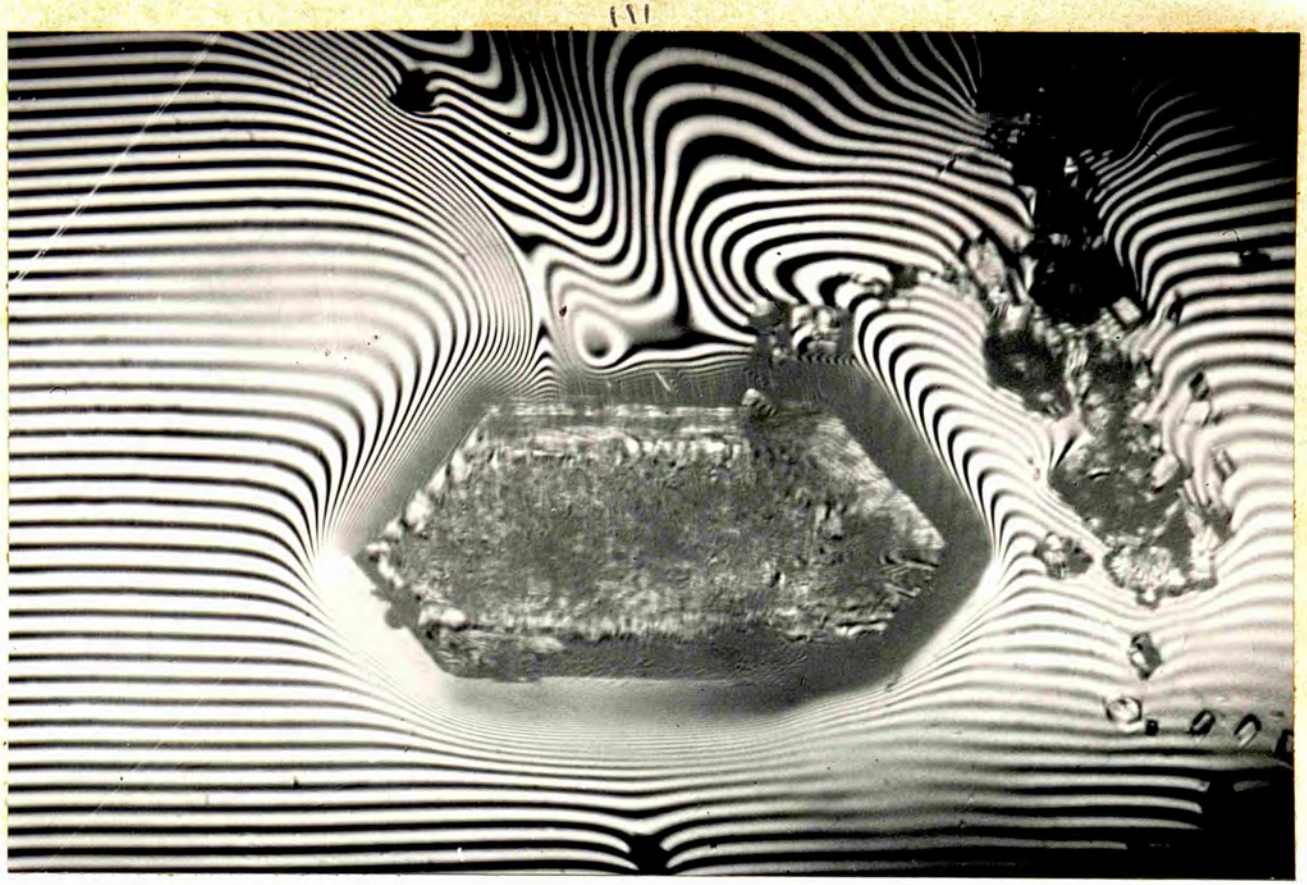


Fig. 6.1.7. Growth after 6 Hrs. 30 Mins. x 24

Crystal 1

The initial concentration of the solution was 77.6%.

The growth of this crystal is illustrated in Figs. 6.1.1 - 6.1.7.

This solution was of fairly strong concentrated and unfortunately nucleation occurred. This could have perhaps been due to any small particles of sugar remaining on the crystal after grinding, care had to be taken to make sure that the surface was as clean as possible.

The streaming was established almost immediately as can be seen in Fig. 6.1.1. There was no marked effect due to dissolution. The concentration gradients can also be seen close to the crystal and unfortunately in many cases these fringes are not resolved. This may be due to the fact that the gradients are so steep that the fringes are too close together to make resolution possible. Alternatively it may be that along different faces the fringes are not all localised in the same plane, parallel to the cell walls, so that only the fringes along one face may be focussed at any one time or the action in the solution may be so vigorous as to destroy the condition for interference fringes. This would seem to be the case along certain faces of this crystal because as time goes on it is possible to distinguish fringes along a face where previously they were not in evidence, e.g. face FA in Fig. 6.1.3.

A few approximate calculations are possible and from these it appears that throughout the period of growth observed, the concentration along the faces FA, EF, and DE remains almost constant. Typical values being 75.6%, 75.6% and 75.1% respectively. The concentration at the corner F always being greater than this and having a value of about 76.4%. The concentration at the bottom face DE is all the time less than at either of the other two faces. This may be due to the fact that the depleted solution is prevented from rising due to the presence of the crystal itself and so is not replaced by fresh, more concentrated, solution.

The value of the concentration down the centre of the stream is 76.6% after 22 mins. and then falls so that at 1 hour, 5 mins. and 2 hours 30 mins. it is 76.3%. So that the solution rising from the growing crystal is still saturated to quite a large extent. Any further measurements after this time cannot be relied on due to the distortion of the fringes above the crystal which results from the presence of the smaller crystals growing in the solution.

Once again the streaming initially from the centre of the top crystal face has moved along the face towards the corner A.

After 6 hours 30 mins. the experiment was discontinued.

TABLE 6.1.

$$\Delta\mu = \Delta n \cdot \frac{\lambda}{t}$$

λ = 5461 Å)
t = 0.183 cms.)
μ_o = 1.4842)

Change in fringe order Δn	Change in refractive index $\Delta\mu$	Refractive index μ	Concentration at face C
9	0.0026	1.4816	76.6%
11	0.0033	1.4809	76.4%
12	0.0036	1.4806	76.3%
13	0.0039	1.4803	76.2%
14	0.0041	1.4801	76.0%
17	0.0050	1.4790	75.6%
18	0.0053	1.4789	75.6%
20	0.0059	1.4783	75.2%
22	0.0065	1.4777	75.1%

Table 6.1. shows the values of concentration calculated for various changes in fringe order. No table is given for the values of concentration at various points along the face as these could only be determined in a few cases.

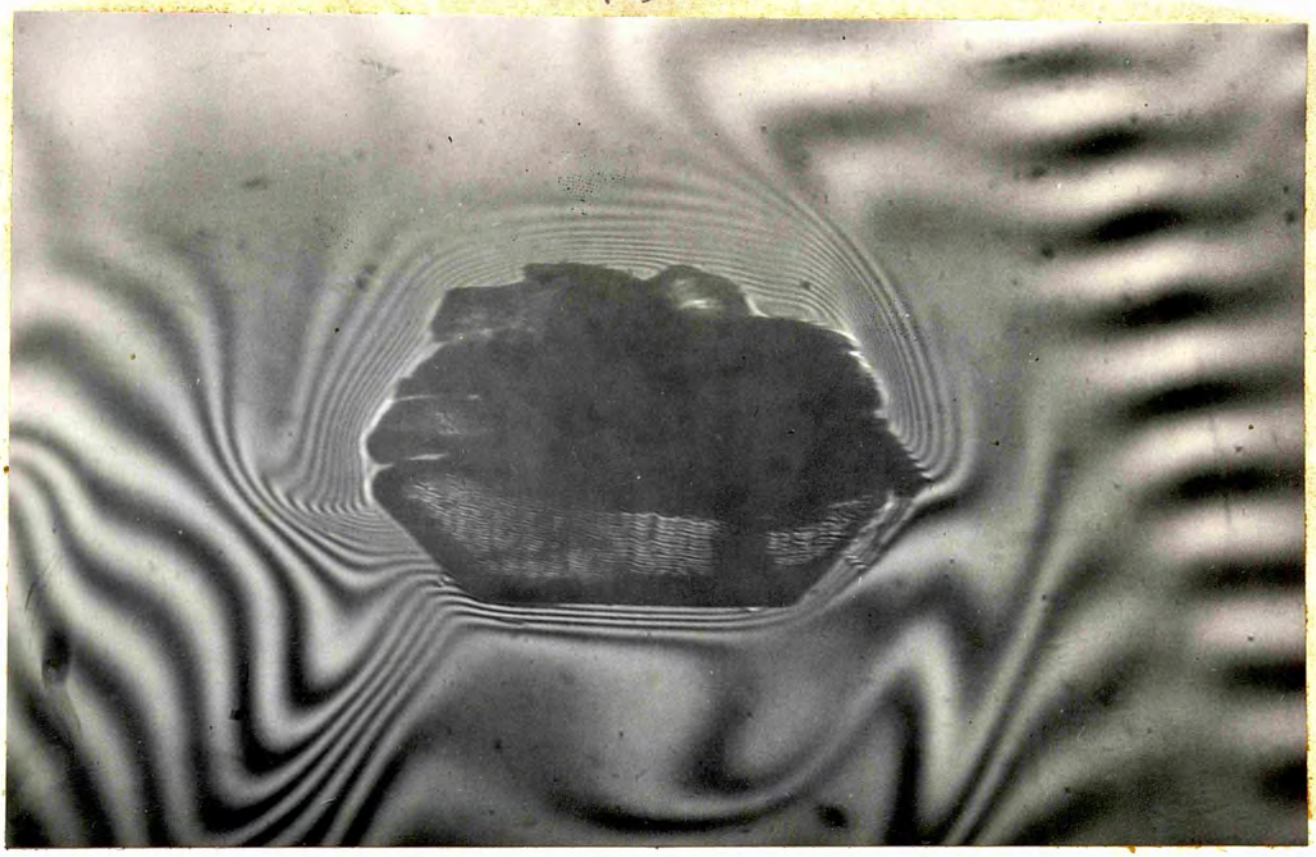


Fig. 6.2.1. Growth after Hrs. 3 Mins. x 22

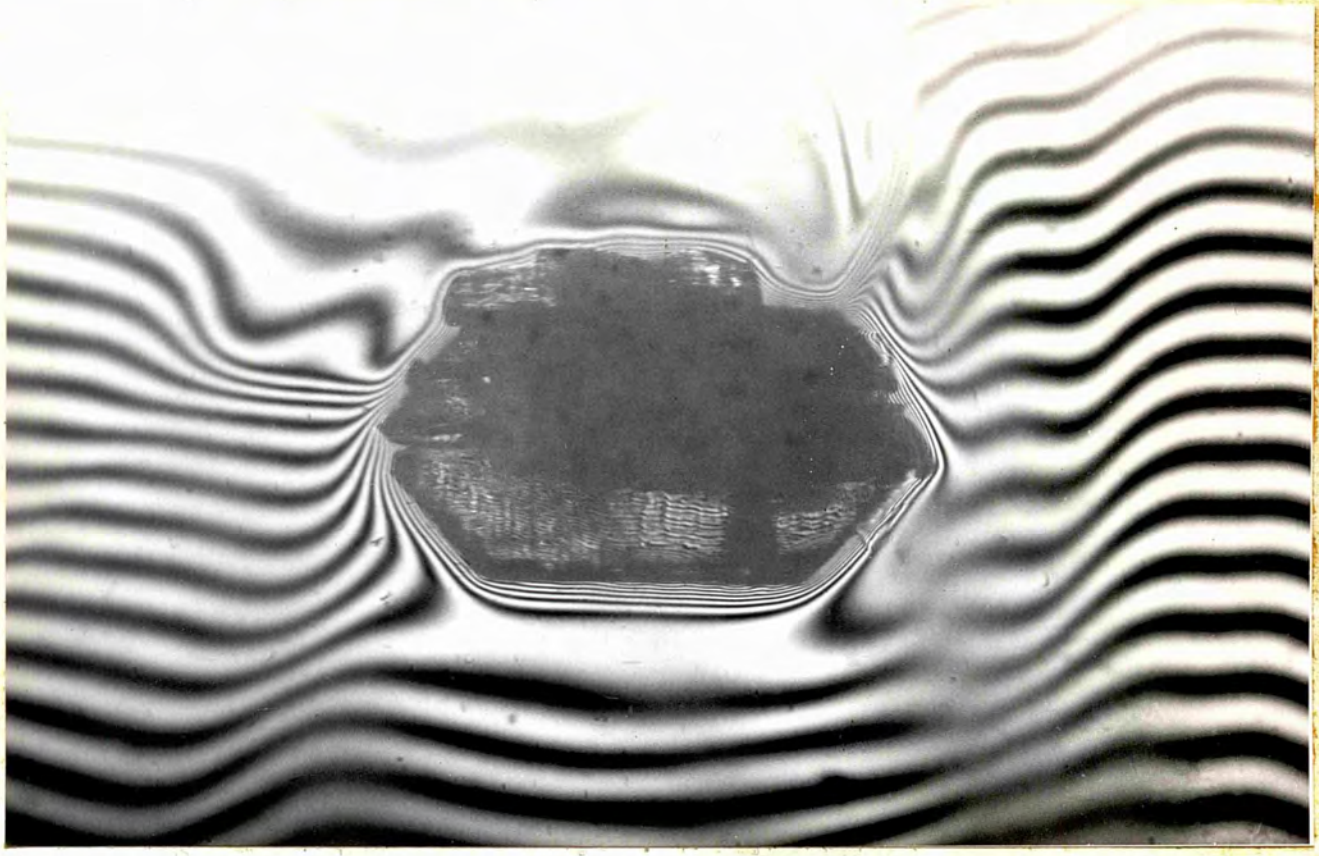


Fig. 6.2.2. Growth after Hrs. 9 Mins. x 22

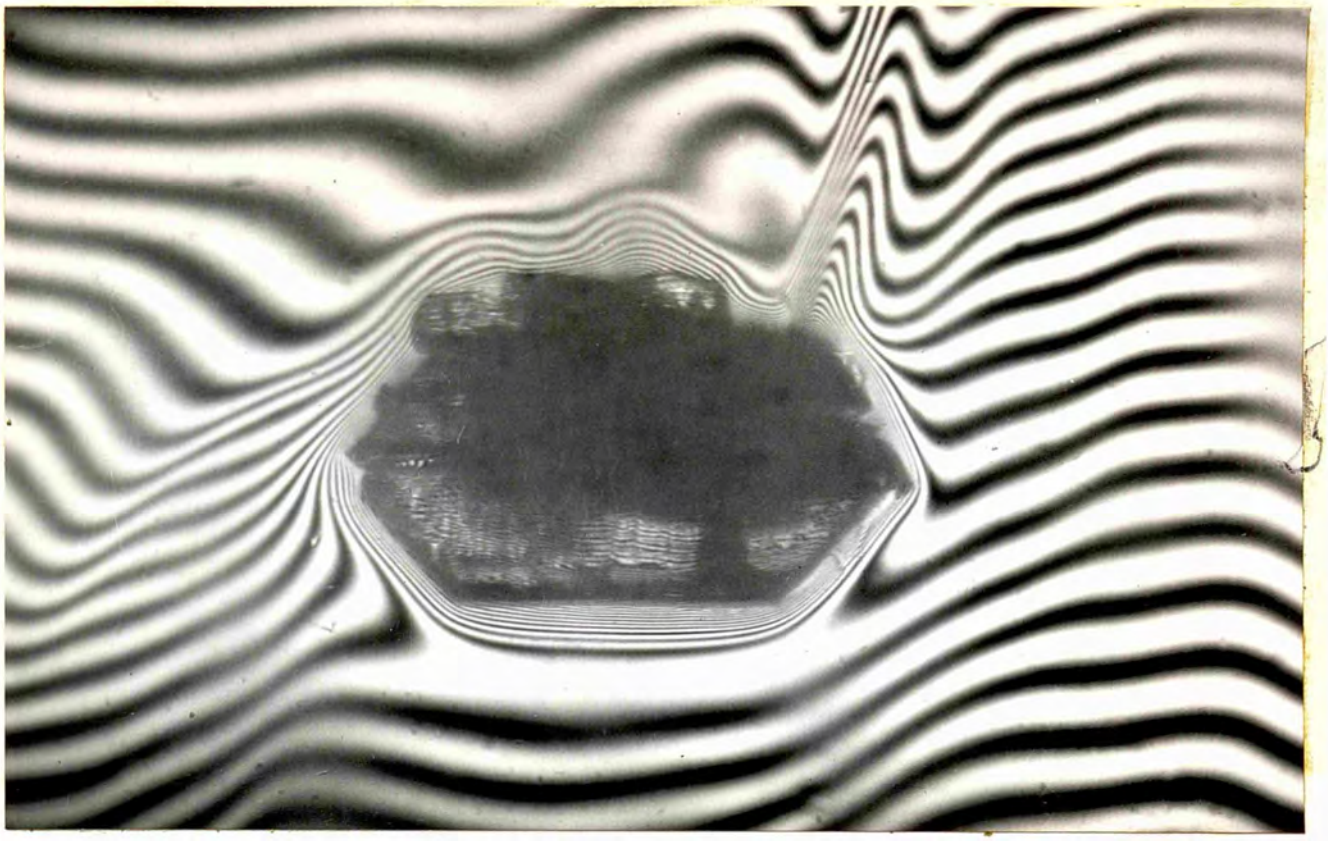


Fig. 6.2.3. Growth after Hrs. 1.5 Mins. x 22

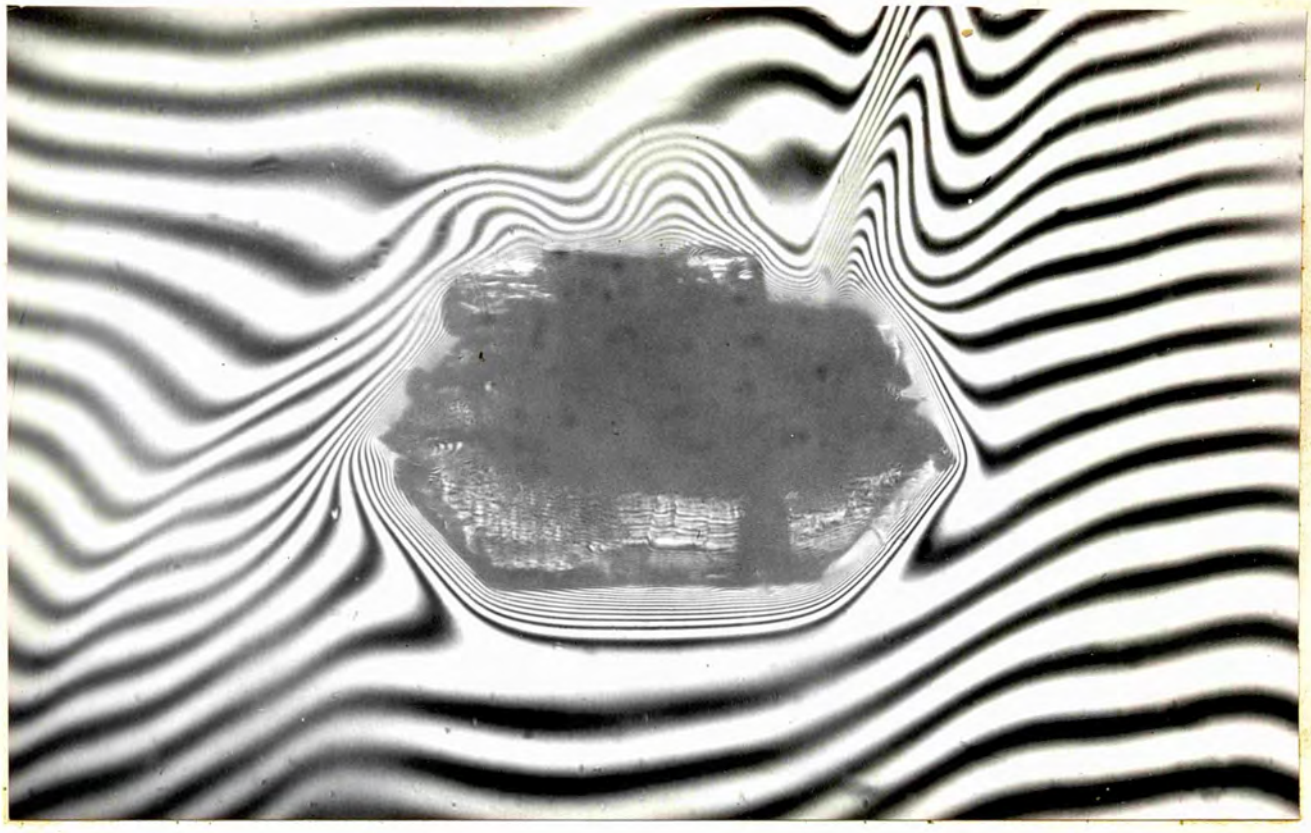


Fig. 6.2.4. Growth after Hrs. 16 Mins. x 22

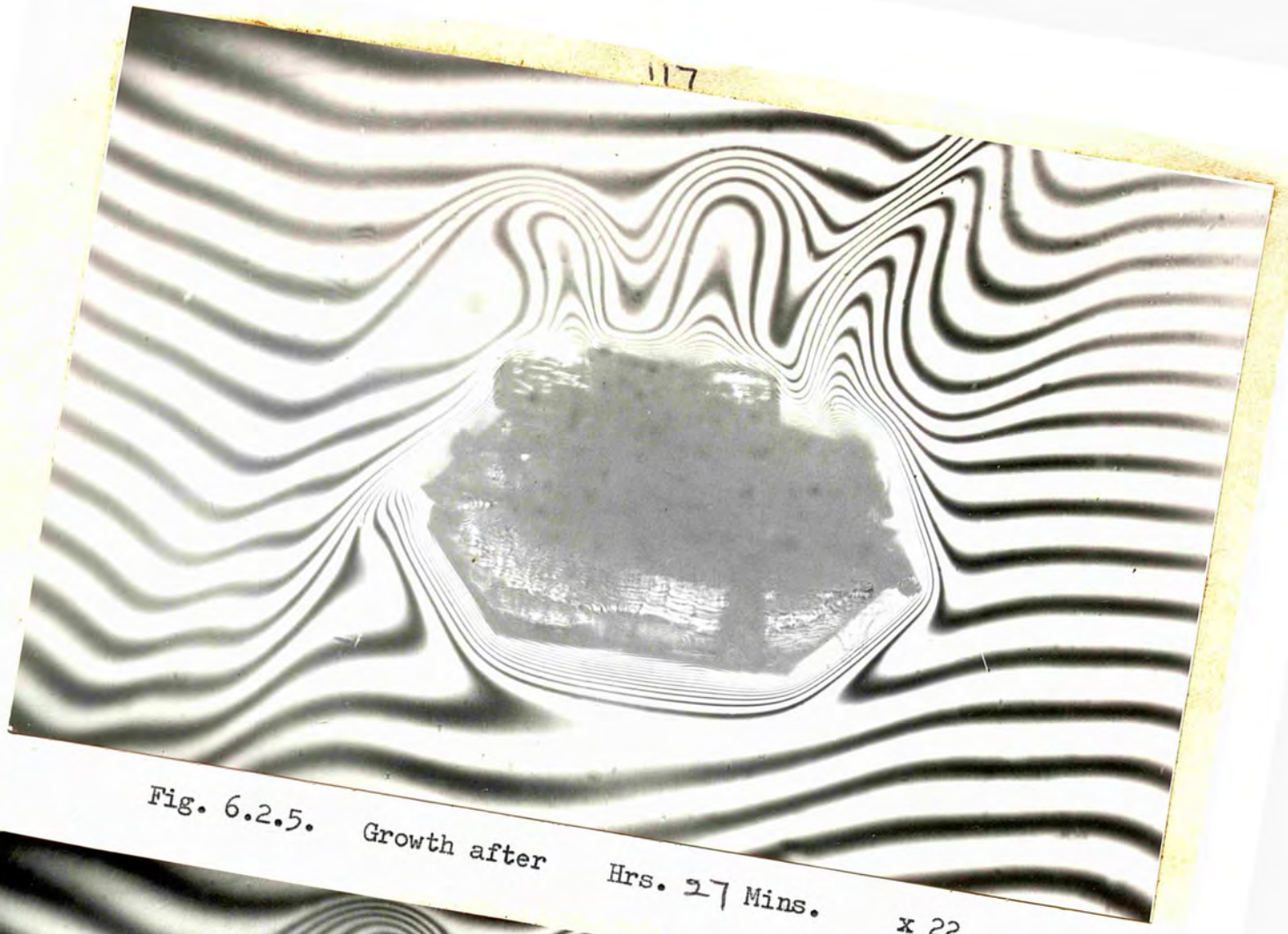


Fig. 6.2.5. Growth after Hrs. 27 Mins. x 22

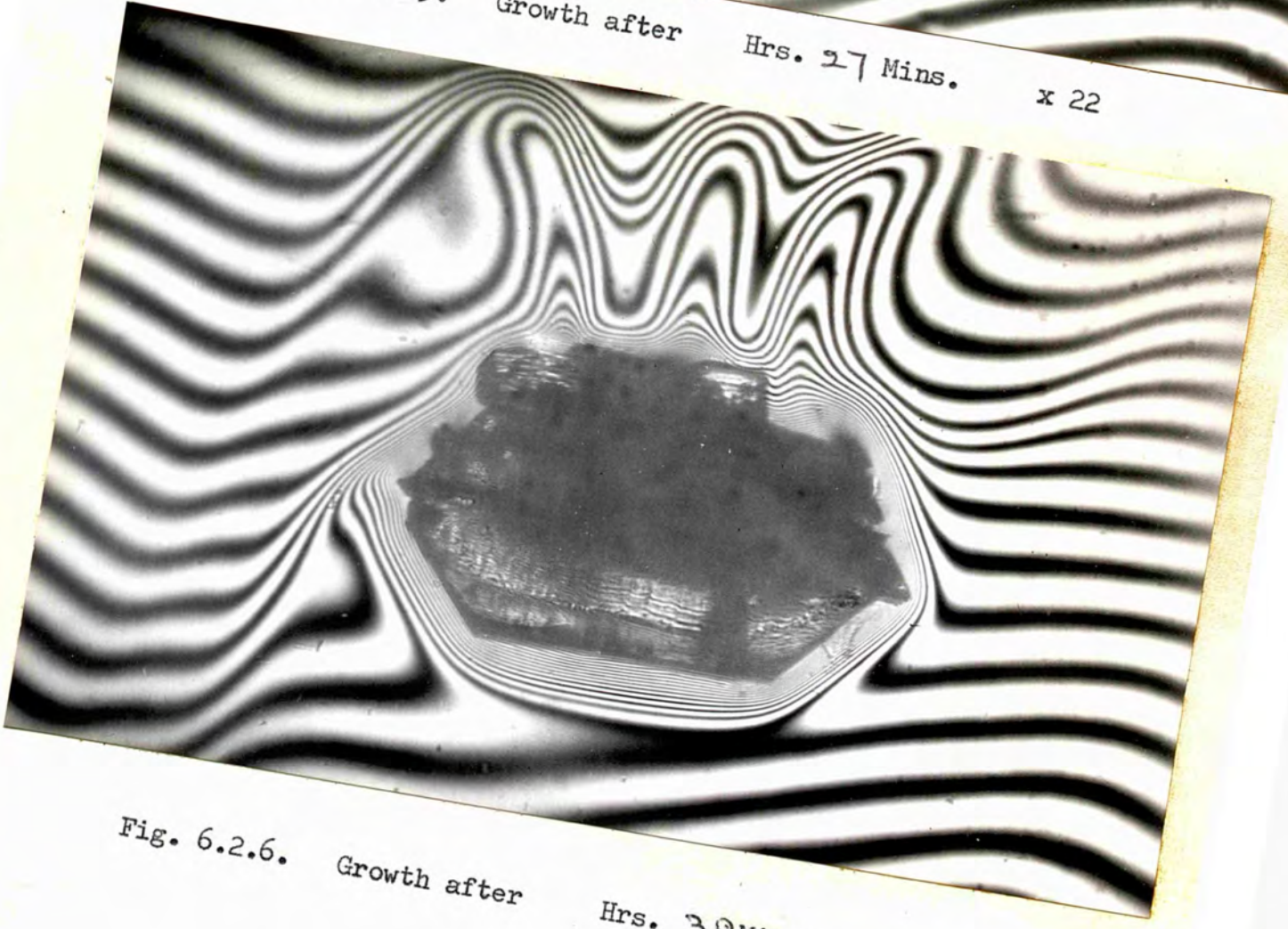


Fig. 6.2.6. Growth after Hrs. 39 Mins. x 22

Fig. 6.2.7. Growth after Hrs. 53 Mins. x 22

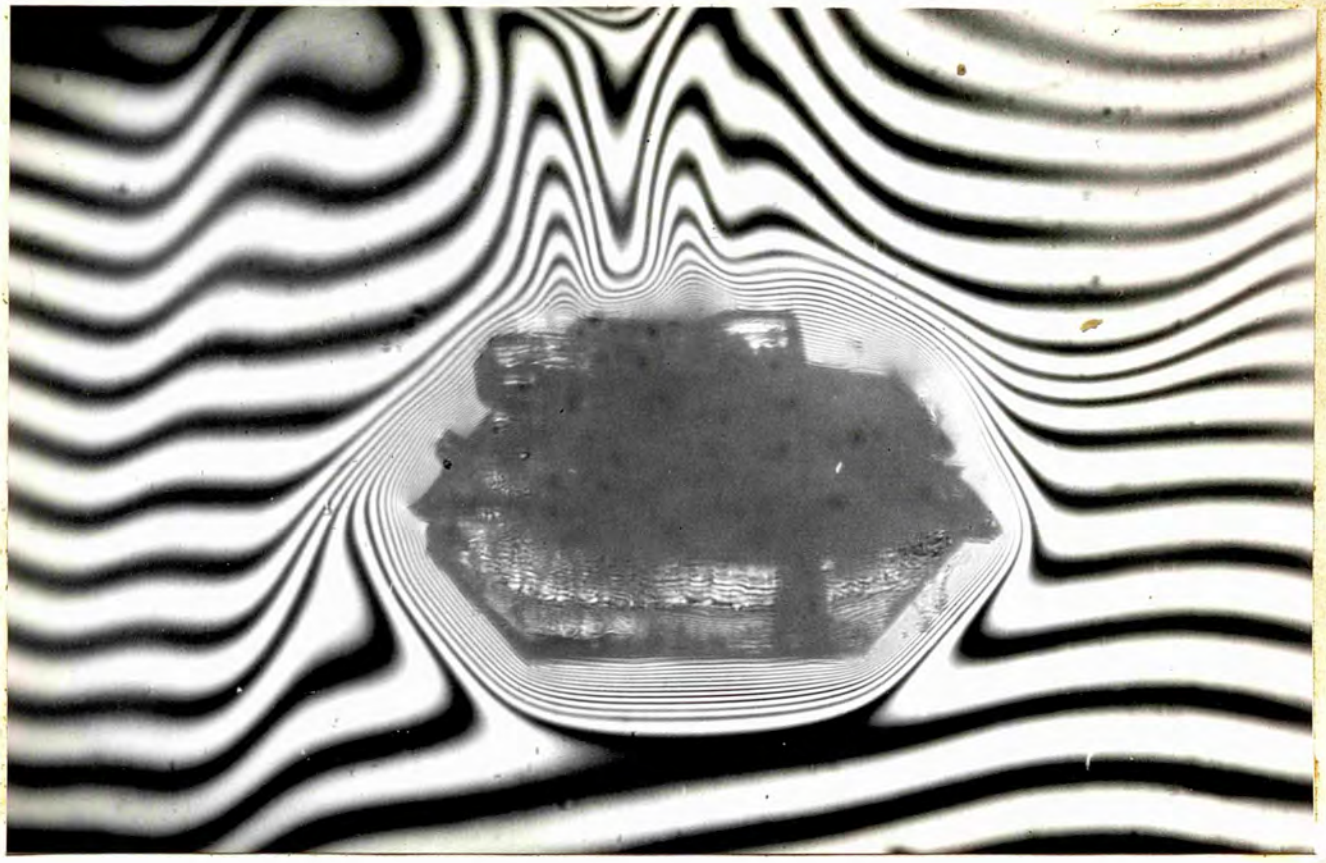


Fig. 6.2.8. Growth after 1 Hrs. 9 Mins. x 22

Fig. 6.2.9. Growth after 1 Hrs. 29 Mins. x 22

Fig. 6.2.10. Growth after 2 Hrs. 0 Mins. x 22

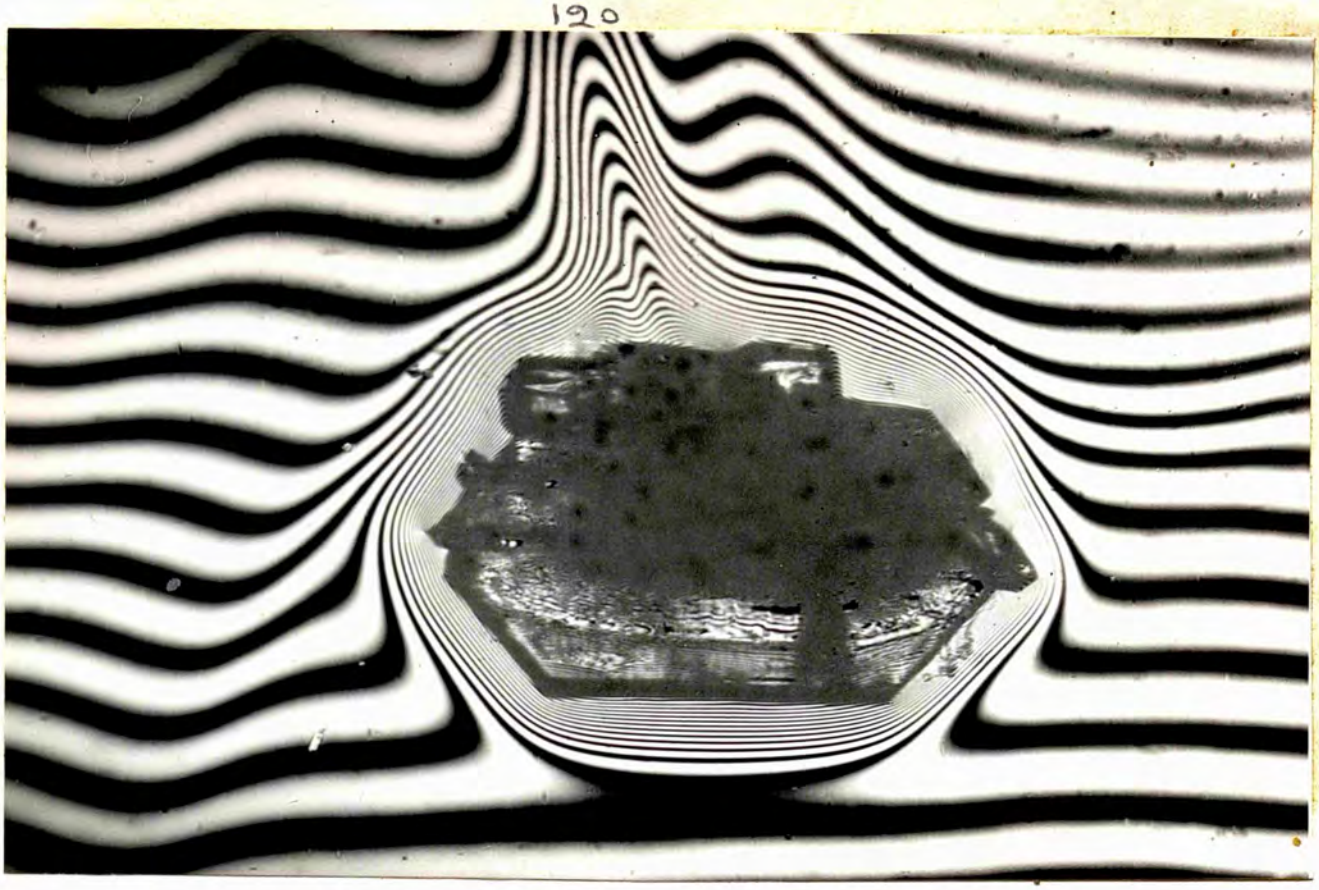


Fig. 6.2.11. Growth after 2 Hrs. 26 Mins. x 22

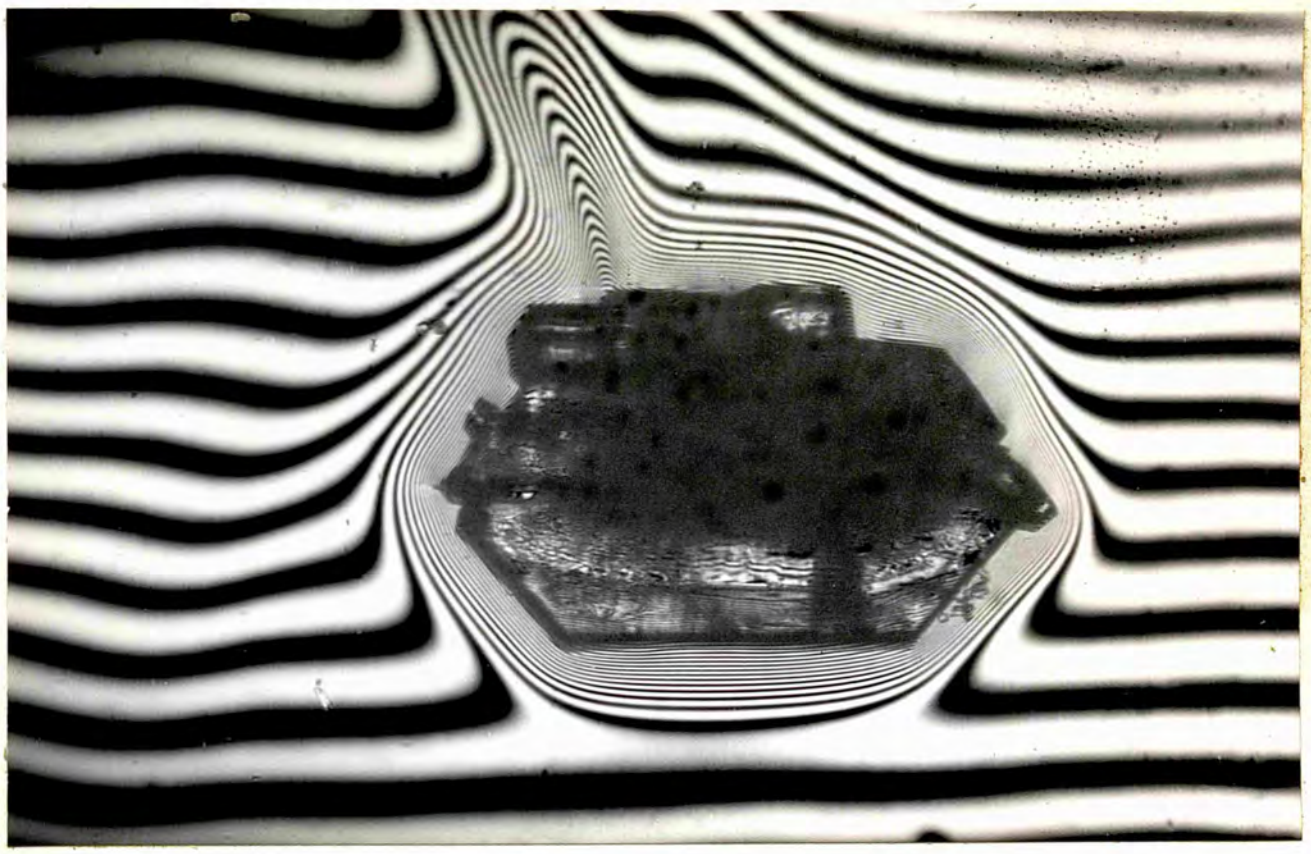


Fig. 6.2.12. Growth after 3 Hrs. 25 Mins. x 22

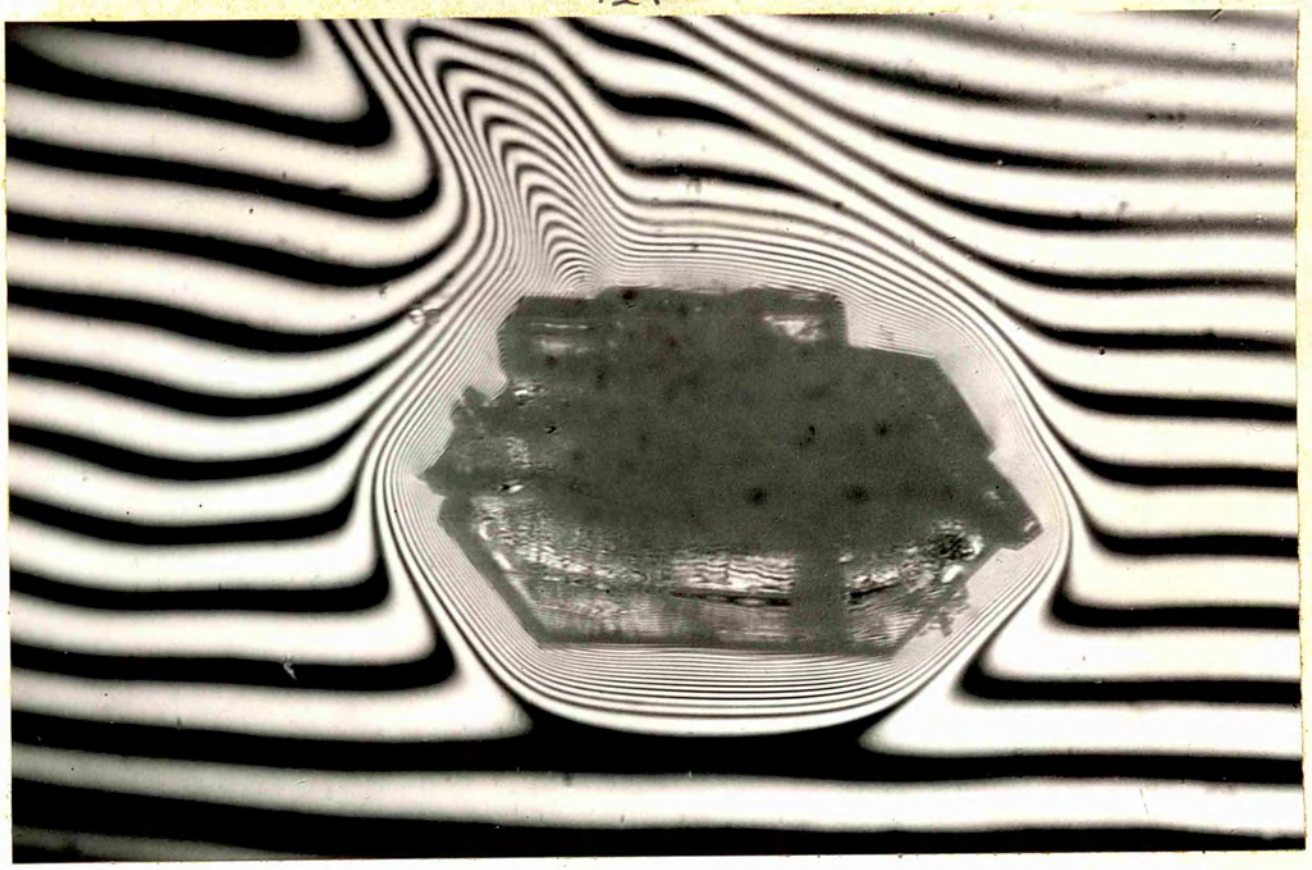


Fig. 6.2.13 Growth after 4 Hrs. 0 Mins. x 22

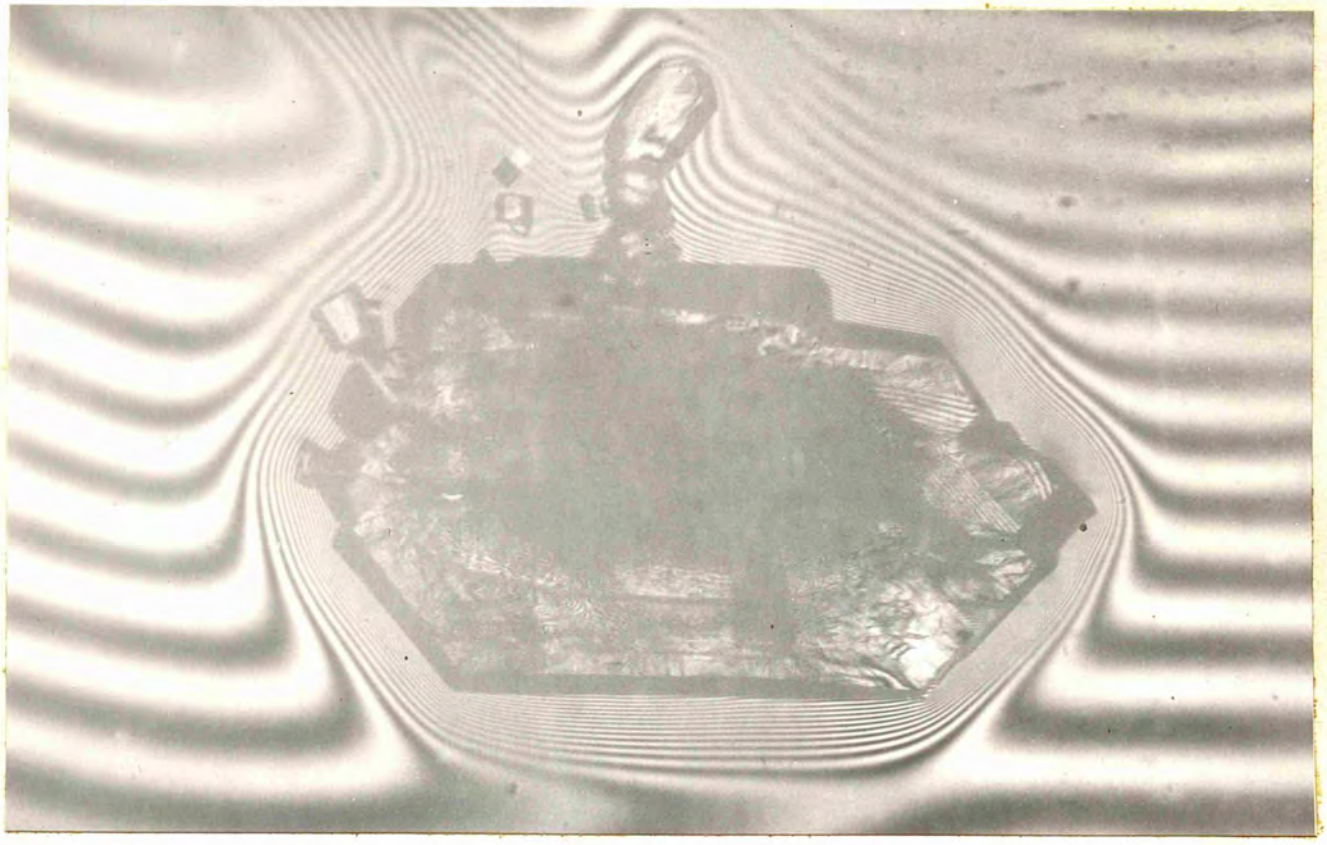


Fig. 6.2.14 Growth after 23 Hrs. 0 Mins. x 22

Crystal 2

The initial concentration of the solution was 75.2%.

The crystal unfortunately broke when the cell was placed in its support. This was hard to avoid, as the crystal was touching the cell walls and any slight pressure could cause it to break.

In the first photograph Fig. 6.2.1. the crystal is in the final stages of dissolution and the fringes are rather distorted. After 9 mins. a slight streaming effect can be seen from the top right hand corner. After 15 mins. there are movements in the solution which would seem to indicate that the depleted solution is trying to rise from other positions along the upper face.

The concentration gradients around the crystal are building up. Table 6.2. shows the values of concentration at the face DE throughout the period of growth observed. No further calculations are possible for the other faces initially, due to the disturbed conditions in the solution. Also along the faces BC and CD the concentration gradient is quite steep and close to the crystal face the fringes have not been resolved, thus eliminating the possibility of any calculation. (They are resolved for face CD in Fig. 6.2.11 and subsequently).

The concentration initially at the centre of face DE when the gradient has become established in Fig. 6.2.2. is 74.6%.

When it is measured again at 15 - 16 mins. it is 74%. By the time the next photograph is taken at 27 mins. it has fallen to 73.8% and this remains constant until at a time of 1 hour 9 mins. it is beginning to rise and has reached a value 73.9%. At 1 hour 29 mins. it has risen to the value 74% and this is maintained for the remaining period of growth.

If these observations on the concentration at the face DE are related to the conditions of streaming in the solution it would appear as if there might be some correlation.

Initially the effects due to convection would be inoperative but a concentration gradient exists and material would travel by diffusion. As the crystal grows the value of the concentration at the face falls to 73.8%. During this time the streaming from the upper surface of the crystal is trying to become established. In Fig. 6.2.8. the single stream is beginning to form and presumably the depleted solution is being removed by convection, (as the concentration has risen to 73.9% and in Fig. 6.2.9 has the value of 74%), and is being replaced by fresh material. As streaming is established any loss of solute to the crystal during its growth can be immediately replaced and the concentration at the face remains constant at the value of 74%.

In Fig. 6.2.12 it is possible to calculate the concentration along the faces CD and EF. For the former the values are 72.8%

at a point just below the outgrowth on corner C and 73.4% at a point just above the corner D. In Fig. 6.2.13. the value has fallen at C to 72.7% and in the next photograph the gradient has once again become too steep so that the fringes are no longer resolved. For the face EF the value is 73.7% along the face which is maintained as growth continues.

In some of the photographs it is possible to see the outline of the original crystal. From this it would appear that originally most of the growth occurred on the faces DE and EF and the upper part of the crystal which is broken appears to be inhibited to a certain extent.

In the final photograph however the face CD has grown out to the greatest extent and this seems to have occurred in the period between 4 hours and 23 hours when the photographs were taken. This face has a very steep concentration gradient contiguous to it and therefore a low value of concentration.

TABLE 6.2.1.

t = 0-173 cms.)
)
μ_0 = 1.4780) in bulk of solution.

Fringe spacing 0.8 cm.

Change in fringe order Δn	Change in the refractive index $\Delta\mu$	Refractive index at the face μ	Concentration at the face.
4.5	0.0014	1.4766	74.65%
5	0.0015	1.4765	74.6%
7	0.0022	1.4758	74.35%
8	0.0025	1.4755	74.2%
9	0.0028	1.4752	74.1%
10	0.0031	1.4749	74.0%
11	0.0035	1.4745	73.8%
12	0.0037	1.4743	73.7%
13	0.0040	1.4739	73.6%
14	0.0044	1.4734	73.4%
18	0.0056	1.4723	72.9%
19	0.0060	1.4720	72.8%
20	0.0063	1.4717	72.7%

TABLE 6.2.2.

	Change in fringe order Δn			Value of Concentration %		
Fig.	Corner E	Centre face	Corner D	Corner E	Centre face	Corner D
6.2.2.	-	5	-	-	74.6	-
6.2.3.	4.5.	10	5.5.	74.65	74.05	74.55.
6.2.4.	4.5.	10	7	74.65	74	74.35
6.2.5.	6	11	9	74.4.	73.8	74.1
6.2.6.	7.5	11	10	74.25	73.8	74
6.2.7.	7.5.	11	10	74.25	73.8	74
6.2.8.	7.5.	10.5	9	74.25	73.9	74.1.
6.2.9.	8	10	9	74.2	74	74.1.
6.2.10.	7.5.	10	7	74.25	74	74.35
6.2.11.	8	10	7	74.2	74	74.35
6.2.12.	8	10	6.5	74.2	74	74.4
6.2.13.	8	10	7	74.2	74	74.35
6.2.14.	9	10	7	74.1	74	74.35

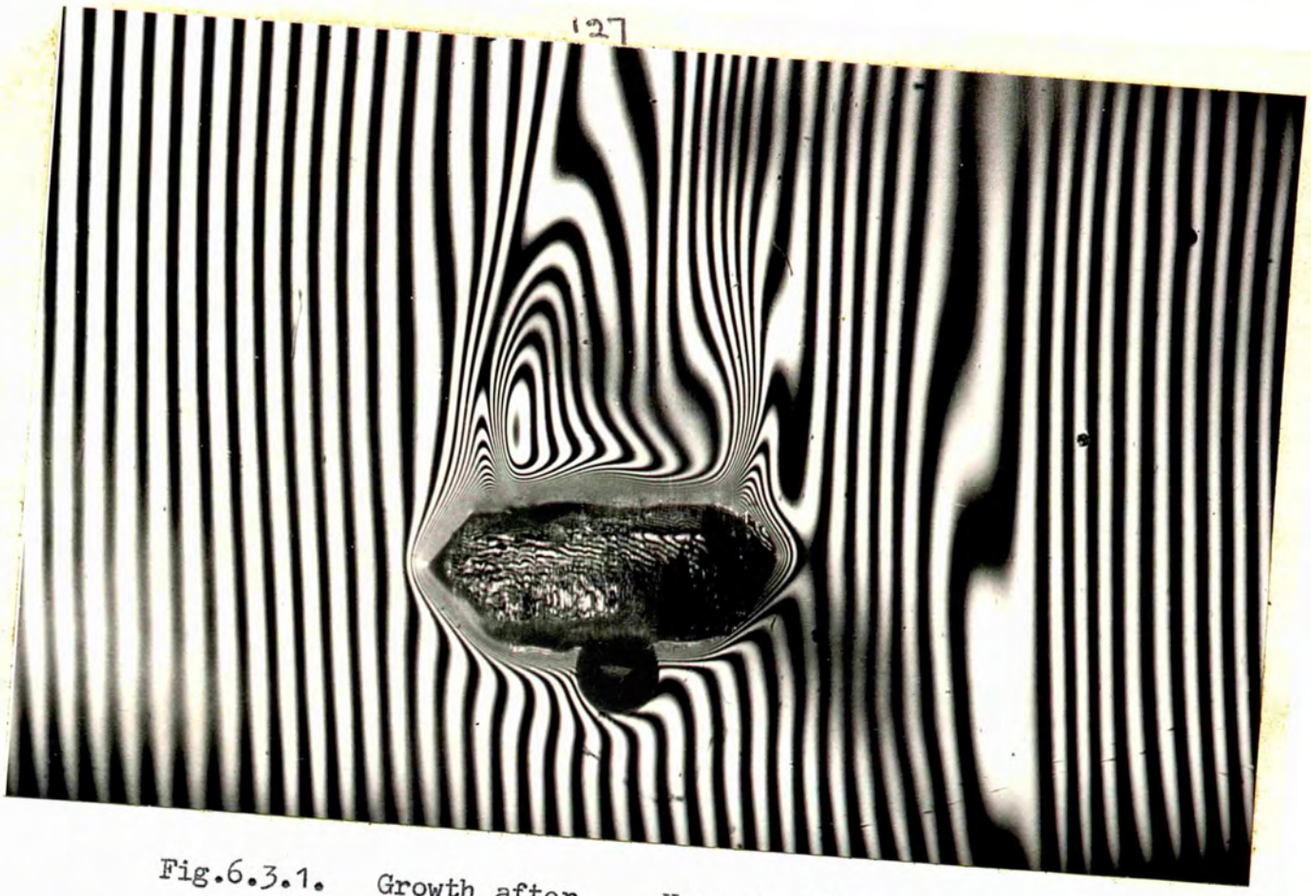


Fig.6.3.1. Growth after Hrs. 16 Mins. x 15

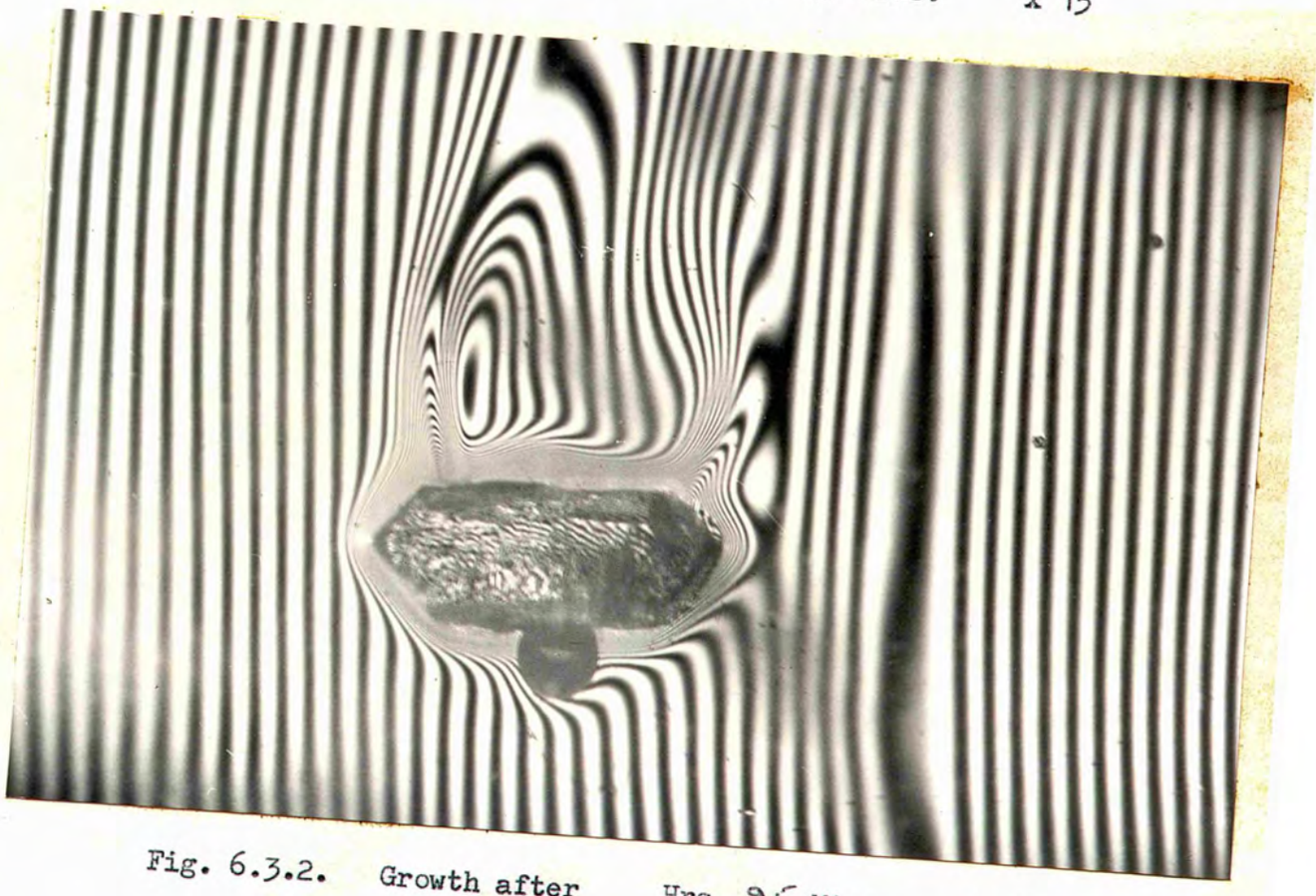


Fig. 6.3.2. Growth after Hrs. 25 Mins. x 15

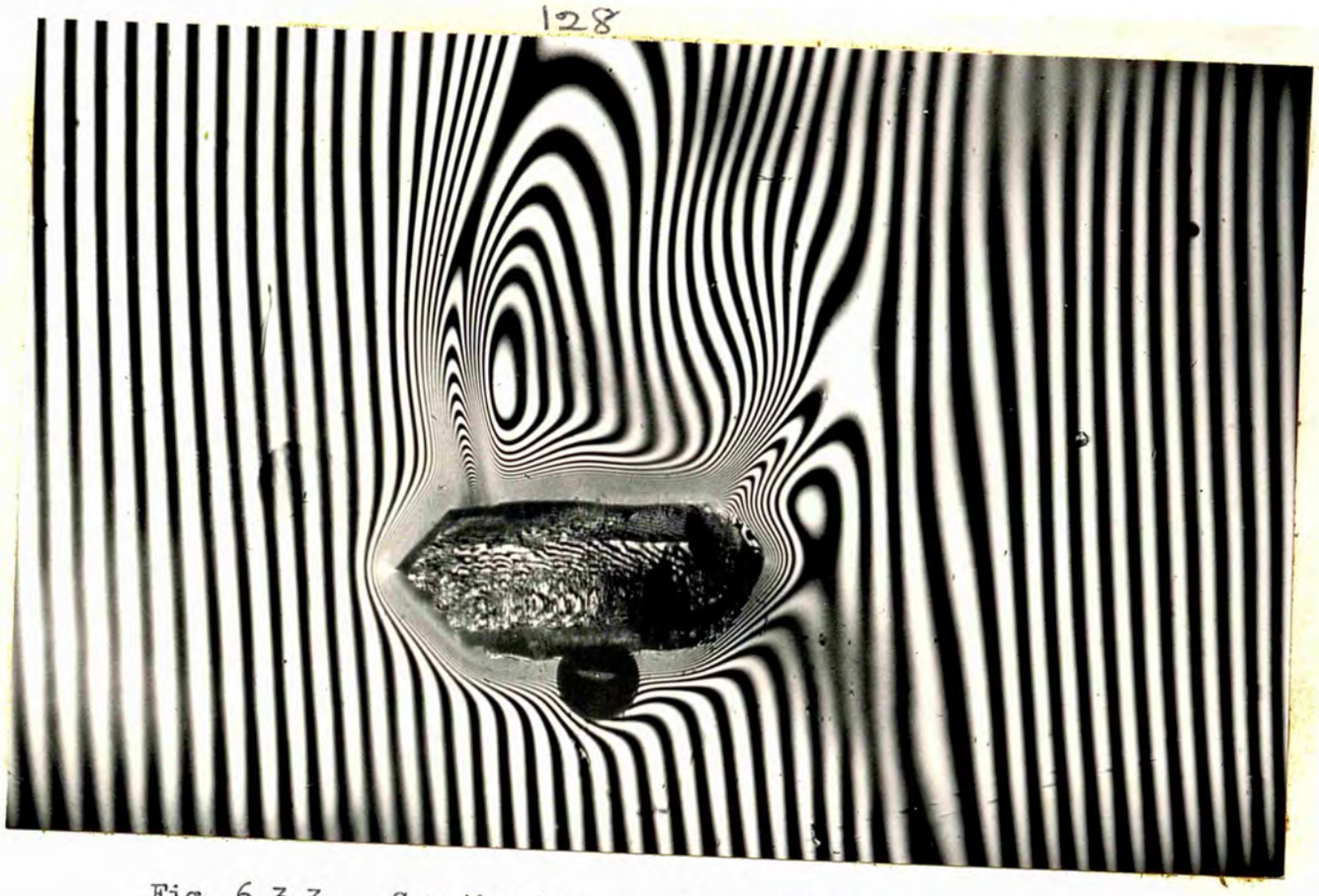


Fig. 6.3.3. Growth after Hrs. 45 Mins. x 15

Fig. 6.3.4. Growth after 2 Hrs. 0 Mins. x 15

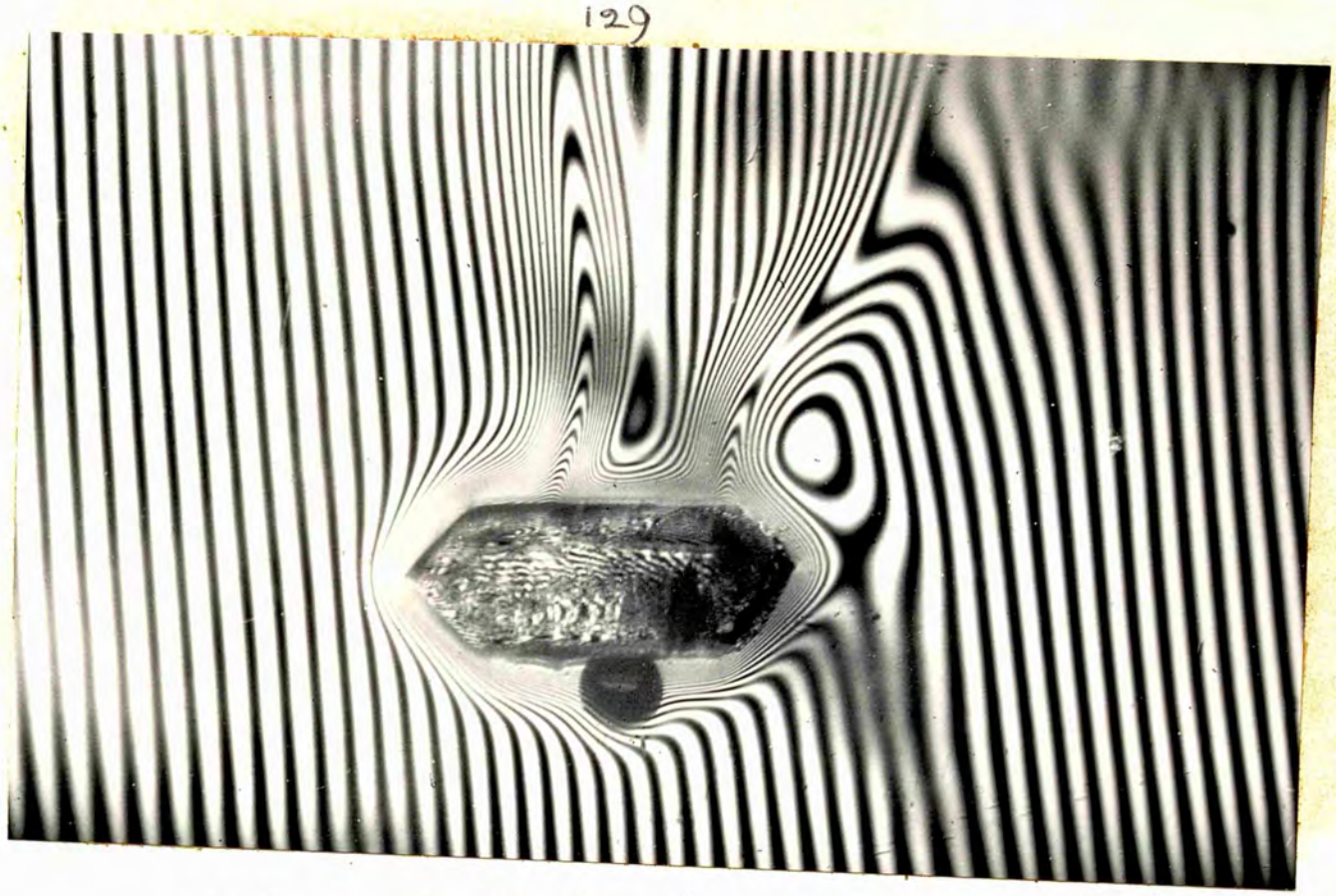


Fig. 6.3.5. Growth after 2 Hrs. 48 Mins. x 15

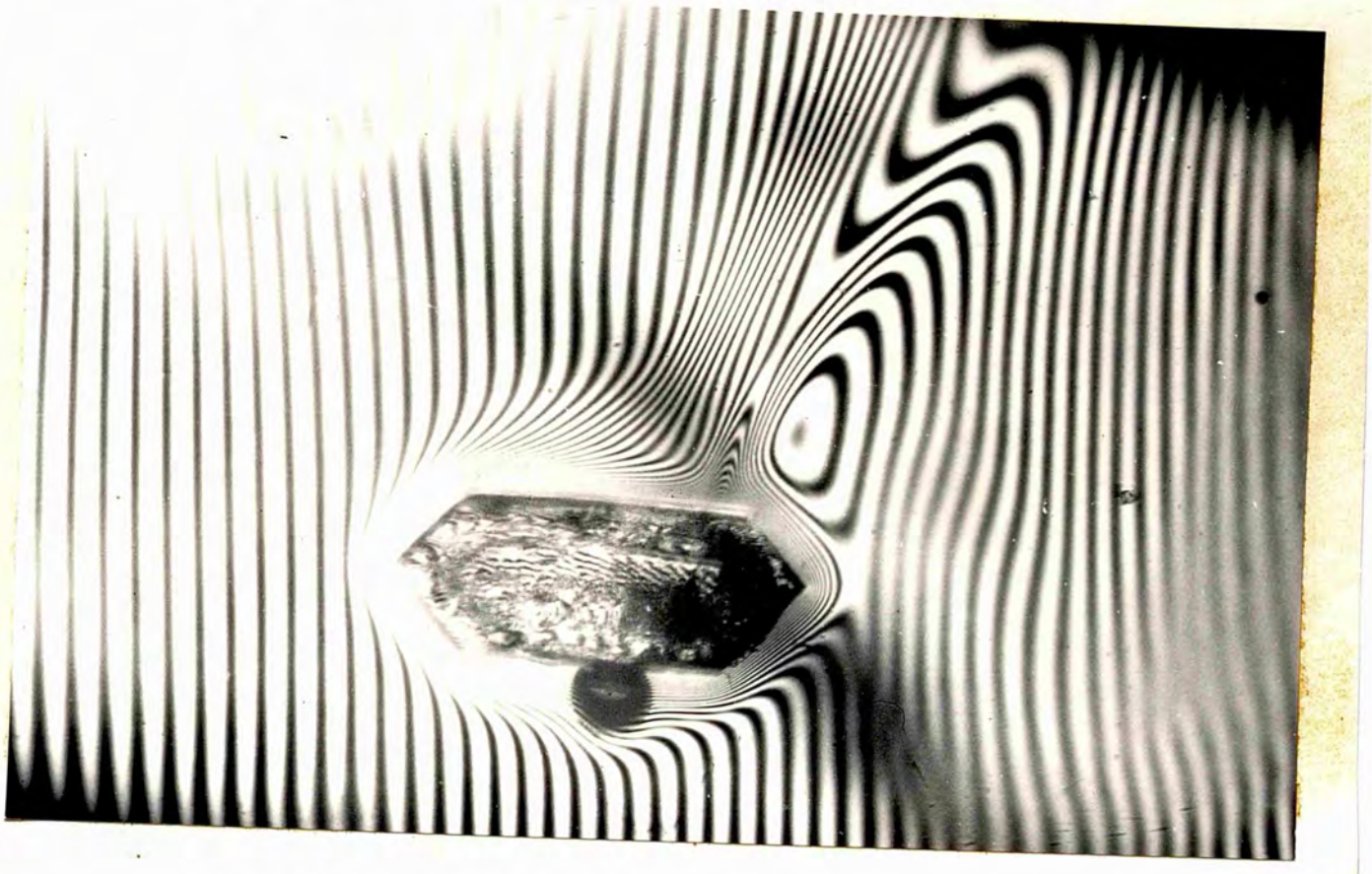


Fig. 6.3.6. Growth after 5 Hrs. 30 Mins. x 15

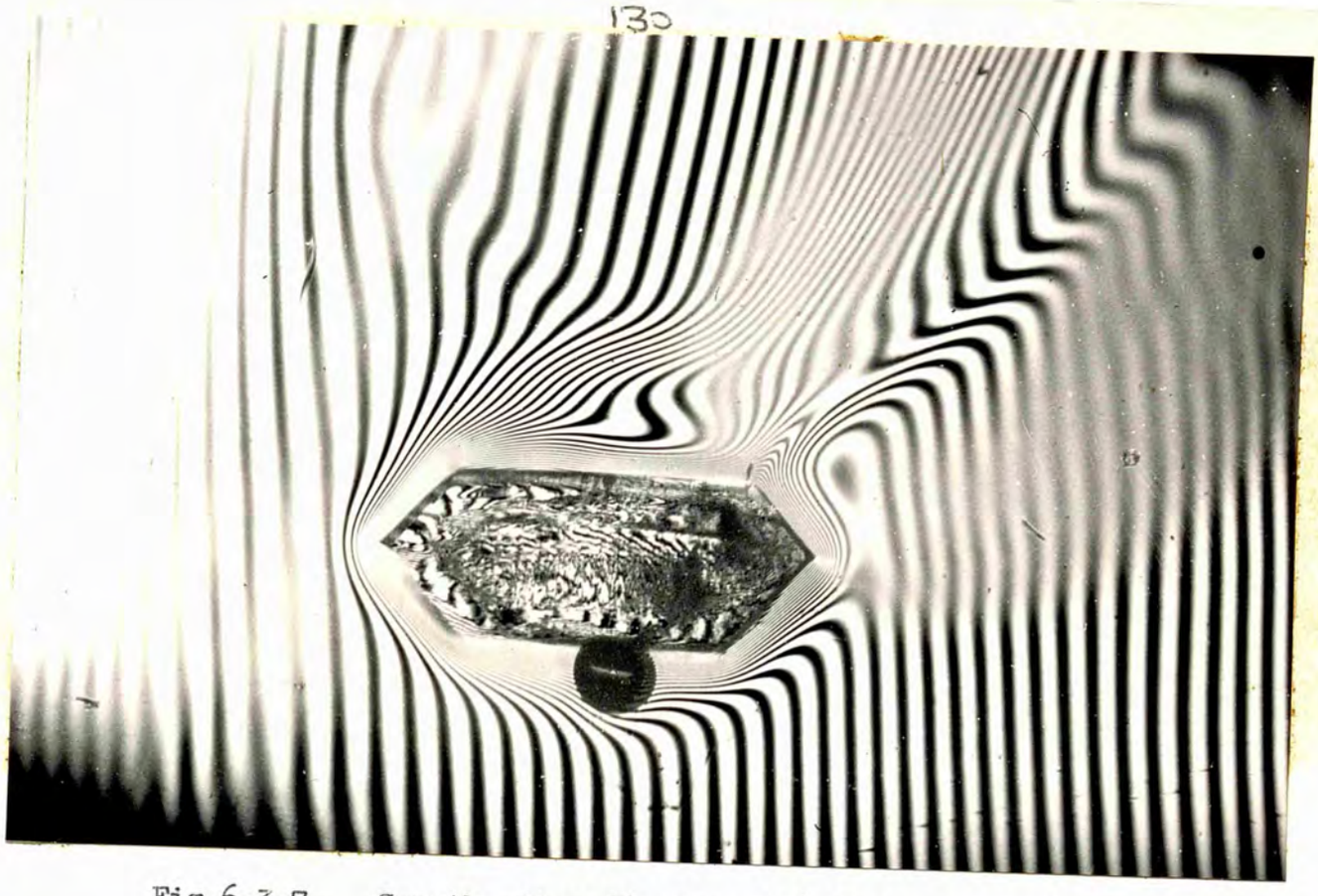


Fig.6.3.7. Growth after 7 Hrs. 25 Mins. x 15

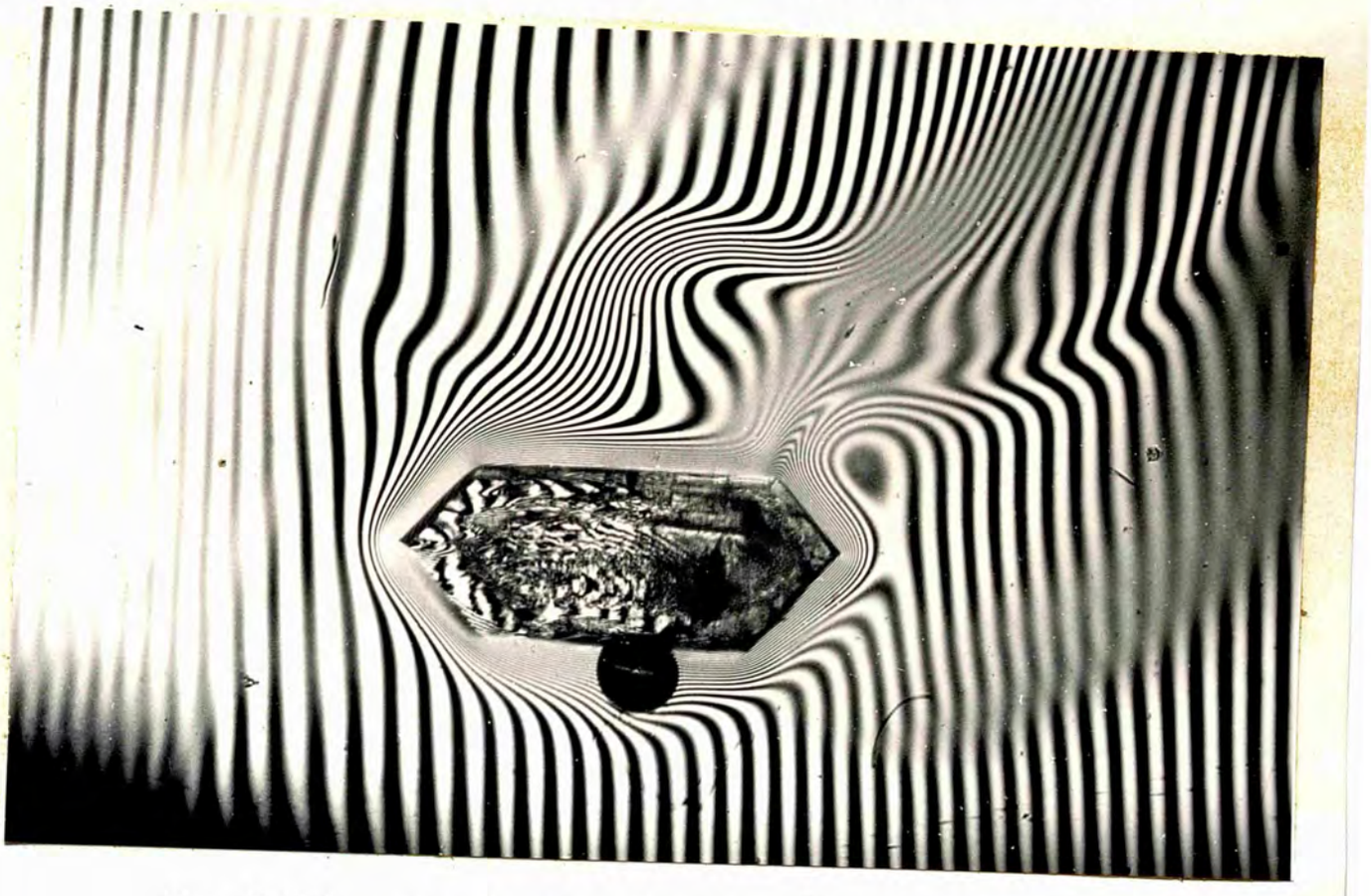


Fig. 6.3.8. Growth after 8 Hrs. 6 Mins. x 15

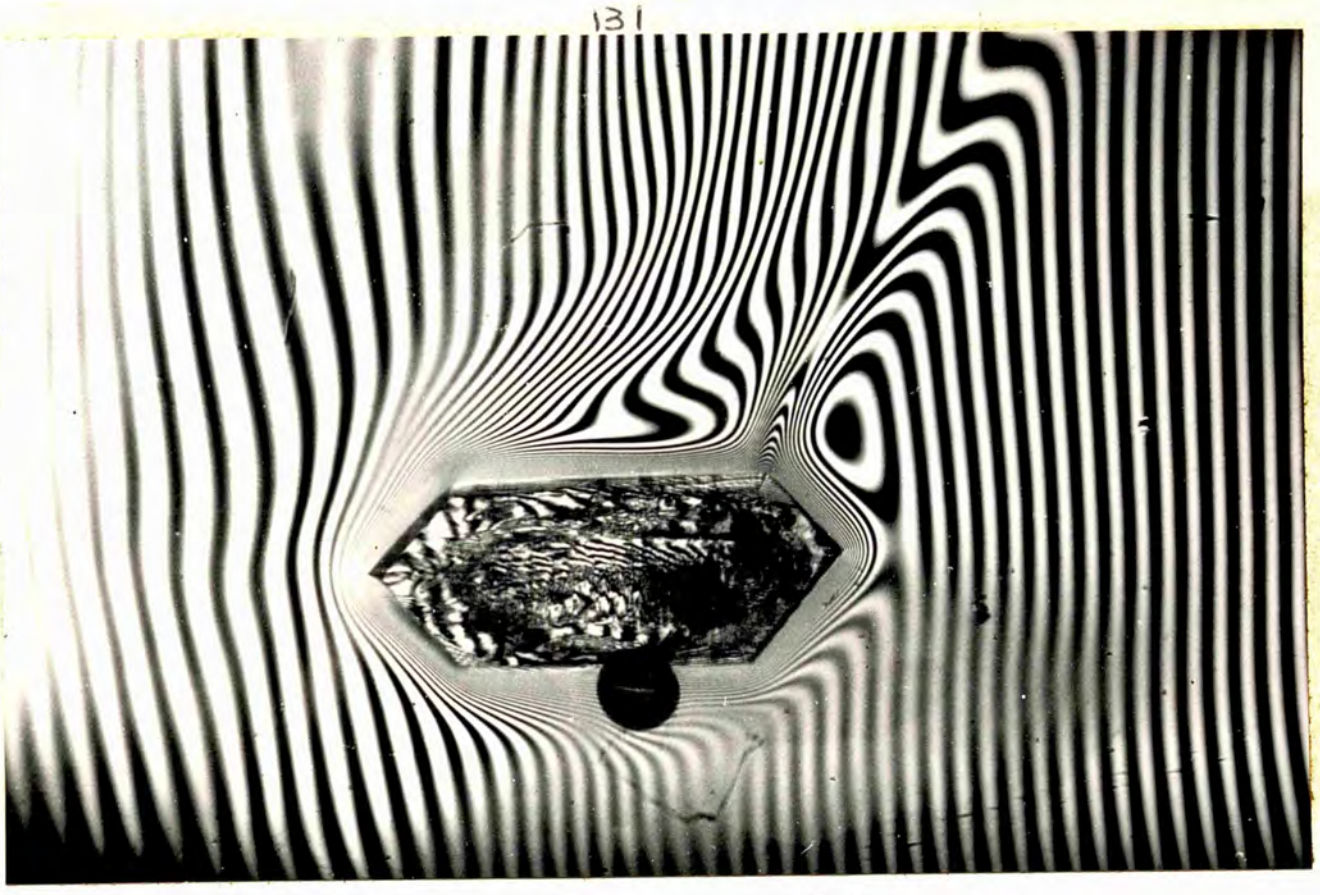


Fig. 6.3.9. Growth after 10 Hrs. 34 Mins. x 15

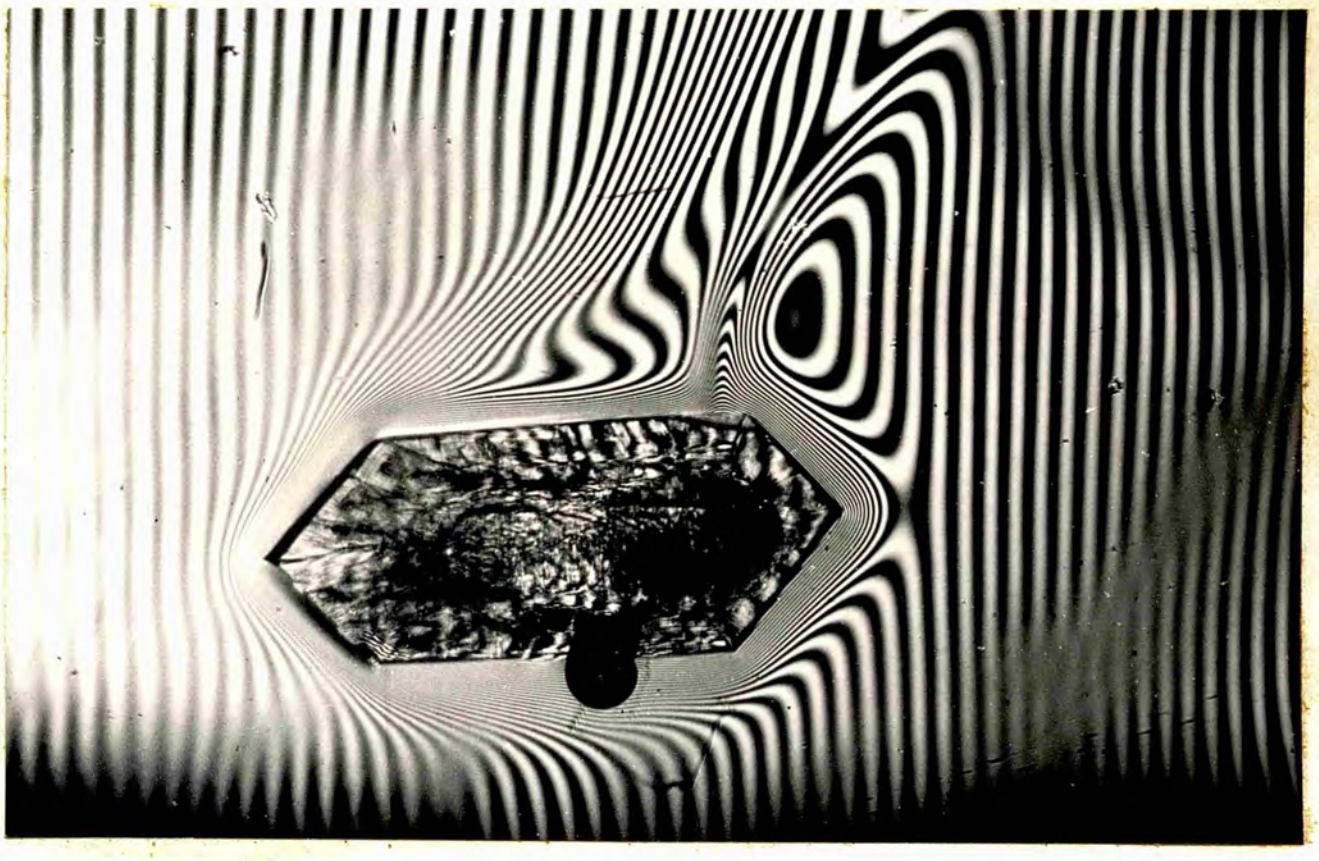


Fig. 6.3.10. Growth after 22 Hrs. 47 Mins. x 15

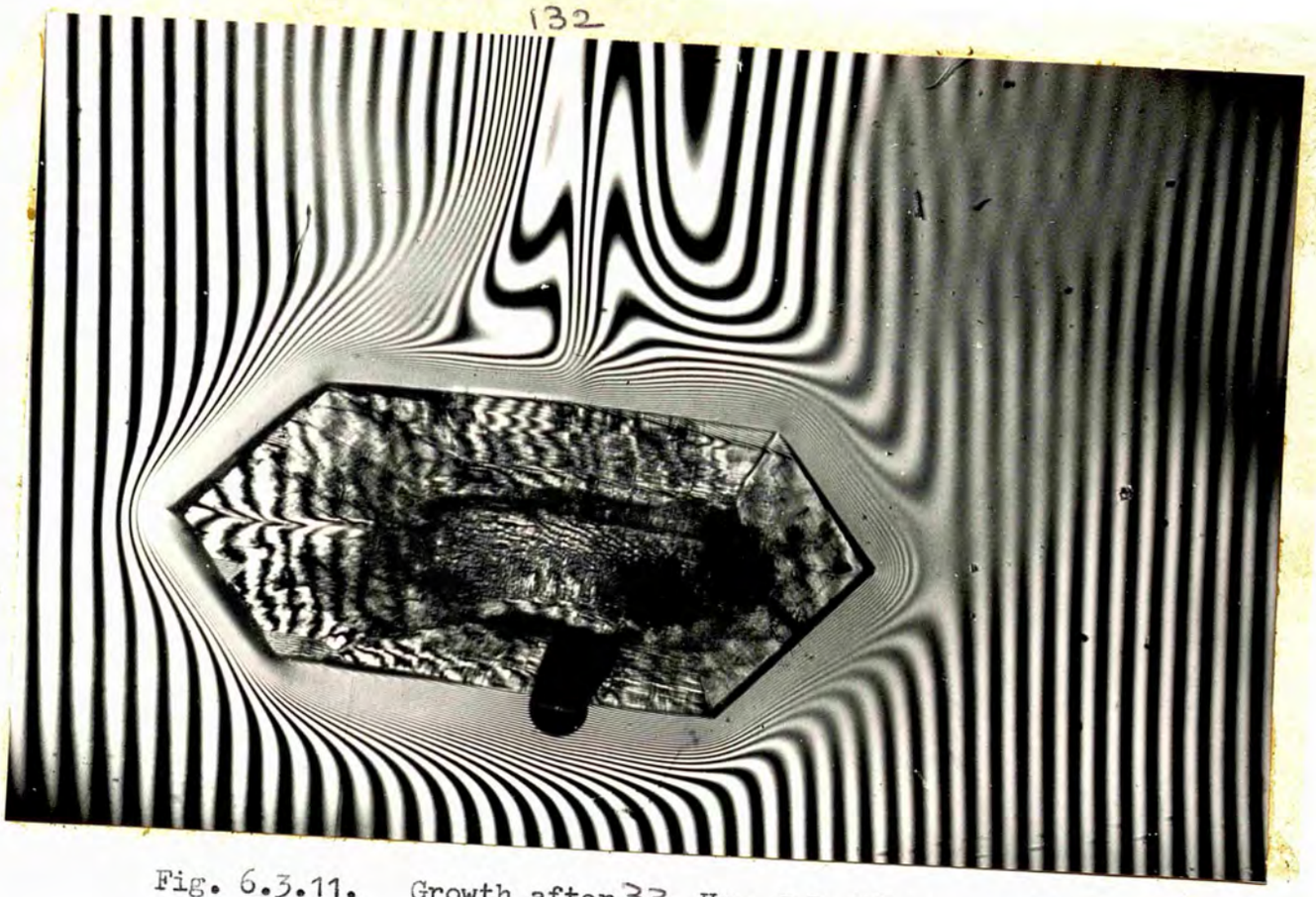


Fig. 6.3.11. Growth after 33 Hrs. 52 Mins. x 15

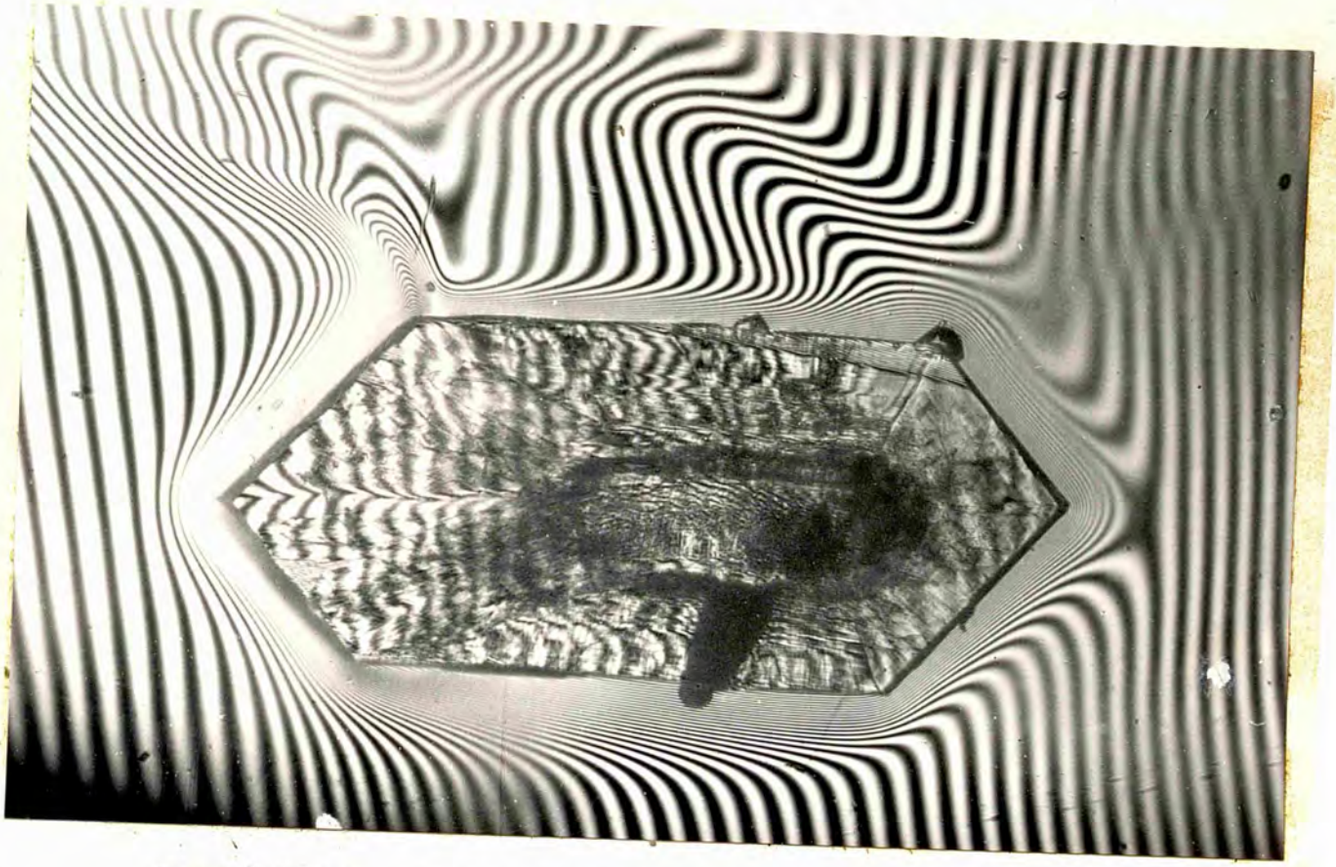


Fig. 6.3.12. Growth after 48 Hrs. 0 Mins. x 15

Crystal 3

The solution in this case has a concentration of 75.7%.

It can be seen that in the first photograph Fig. 6.3.1. taken 16 mins after the start that streaming is taking place from the corners A and B. (The black spot on the face DE is an air bubble which became lodged when the solution was poured into the cell and could not be removed. During growth this has been incorporated into the crystal). The streams from A and B are initially both vertical. The one from corner B does appear to be tending to move along the face BC for a short distance but in Fig. 6.2.4 it is again established at the corner. The stream from corner A moves along the face AB, as time goes on, until in Fig. 6.3.6. 5 hours 33 mins. after growth commenced it has combined with that from B. In Fig. 6.3.7. at a time of 7 hours 25 mins. conditions in the solution above the crystal are undergoing a further change and the streaming vertically upwards appears less strong. Later on in Fig. 6.3.9. it appears to have re-asserted itself. In Fig. 6.3.11 distinct streaming in the normal pattern is no longer in evidence but in the final photograph taken 14 hours later the streaming is taking place from corner A.

An important connection, in studying the growth of crystals, would appear to exist between the rate of growth of a crystal and the conditions in the solution. Unfortunately in the present

situation it was not possible to measure the rate of growth of individual faces with any accuracy. In an effort to overcome this difficulty it was decided to measure the increase in area of the crystal with time. This was done using a planimeter. The present crystal was the only one, with a sufficiently well defined perimeter, to produce consistent results. By this means it was thought possible to connect the rate of growth of the crystal with the streaming effect. The result is produced graphically in Fig. 6.3.13. The length of the horizontal lines in the graph represents the average rate of growth over the period of time for which this has been measured i.e. between the period of time from 33 hours 52 mins. to 48 hours the average rate of growth was 5.12×10^{-1} sq. cms/hour. The mid points of these lines have then been joined.

It can be seen that initially there is quite a fast rate of growth but this falls to its minimum value 1.31×10^{-1} sq. cms/hr. during the time that the streaming is trying to become established. By the time that streaming has become established at a time of 5 hours 30 mins. the growth rate has increased to 2.20×10^{-1} sq. cms/hour. After this time the streaming becomes disturbed and this seems to have had an effect on the rate of growth which again decreases. Streaming is again established at a time of 10 hours 34 mins. and during this time the growth rate has increased to the

value 3.74×10^{-1} sq. cms/hour. The fall in the growth rate over the next 12 hours is not explained by this. This occurred overnight and perhaps if more photographs had been obtained during this period an explanation could have been obtained. During the period of time between the last two photographs when the streaming has been disturbed and become established at the corner A there has again been a decrease in the rate of growth.

One effect that was noted during the early stages of growth was that at the corners C and F, where light spots can be seen due to some vigorous action in the solution. These are especially clear for corner F in Figs. 6.3.3. and 6.3.4. This was observed for several crystals and it sometimes appeared as if just that point was growing.

Once again in several of the photographs the faint outline of the original crystal can be distinguished. In Fig. 6.3.7. all the faces seemed to have extended by approximately the same amount except the lower face DE which appears to have been prevented from growing by the presence of the air bubble, even though there is quite a large gradient of concentration adjacent to it. The concentration along the face during this time is approximately 73.65%. but in Fig. 6.3.10 when it can be seen that the face has started growing it has fallen to a value 73.25%.

During the 12 hours between the taking of photographs

6.3.9. and 6.3.10. the faces EF and FA have obviously grown more than the others and this is clearly seen by the end of the experiment. Once again these faces have the steepest gradients adjacent to them as the fringes have not been resolved.

TABLE 6.3.

Time Hrs.	Time Mins.	Time interval Hrs.	Time interval Mins.	Vernier Reading V	δV	Average Rate of growth. sq.cms/hr.
-	16			0.650		
		-	9		0.01	3.99×10^{-1}
-	25			0.660		
			20		0.03	5.94×10^{-1}
-	45			0.690		
		1	15		0.04	2.11×10^{-1}
2	0			0.730		
			48		0.02	1.31×10^{-1}
2	48			0.750		
		2	42		0.09	2.20×10^{-1}
5	30			0.840		
		1	55		0.06	2.07×10^{-1}
7	25			0.900		
			41		0.02	1.93×10^{-1}
8	6			0.920		
		2	28		0.14	3.74×10^{-1}
10	34			1.060		
		12	13		0.54	2.92×10^{-1}
22	47			1.600		
		11	5		0.96	5.72×10^{-1}
33	52			2.560		
		14	8		1.11	5.12×10^{-1}
48	0			3.670		

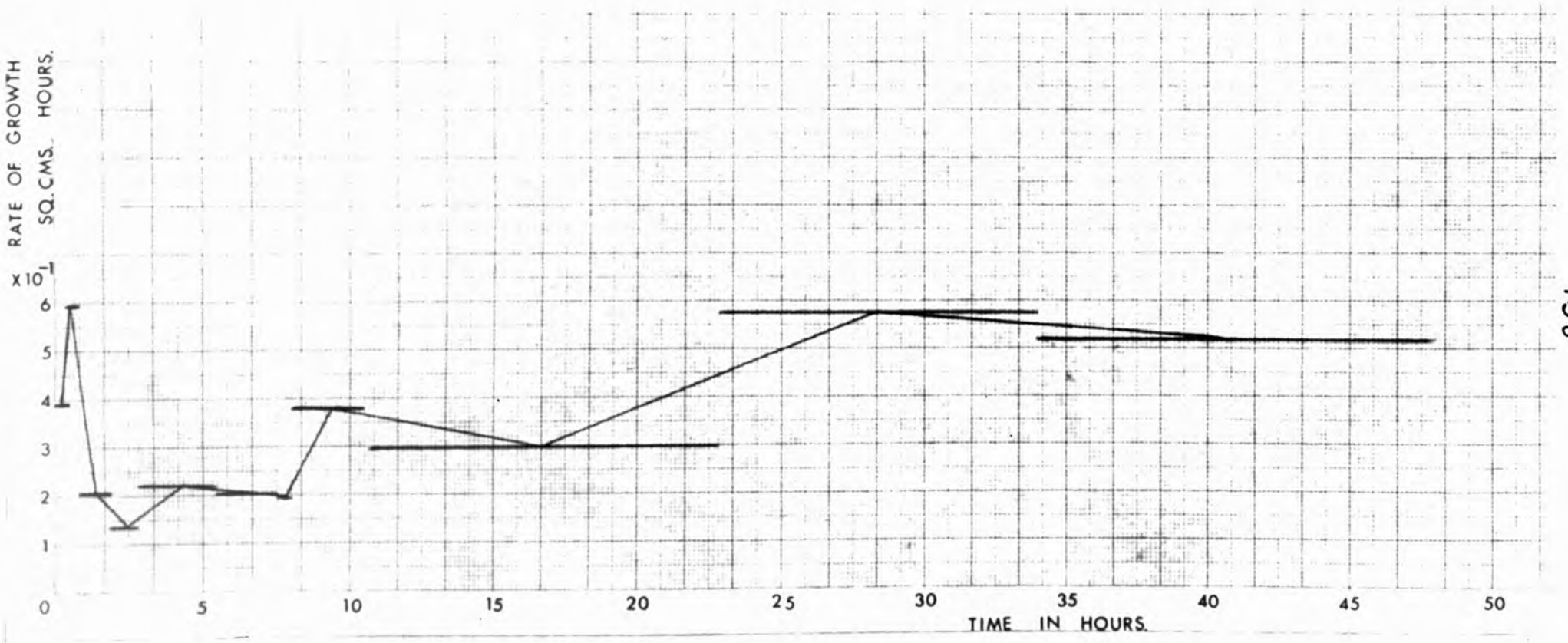

RATE OF GROWTH
SQ.CMS. HOURS.
x 10⁻¹
6
5
4
3
2
1
0
5
10
15
20
25
30
35
40
45
50
TIME IN HOURS.

Fig 6.3.13.

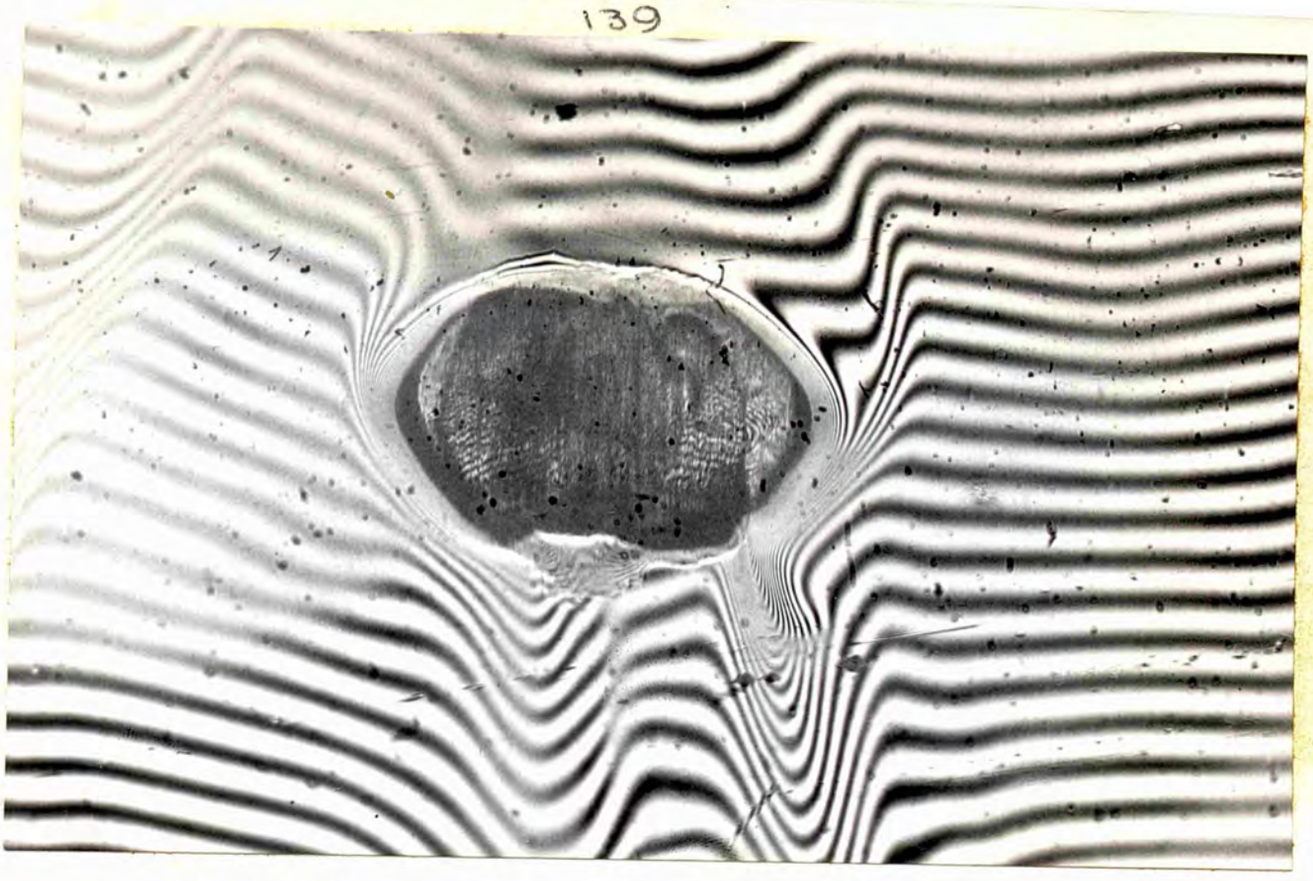


Fig. 6.4.1. Growth after Hrs. 6 Mins. x 19

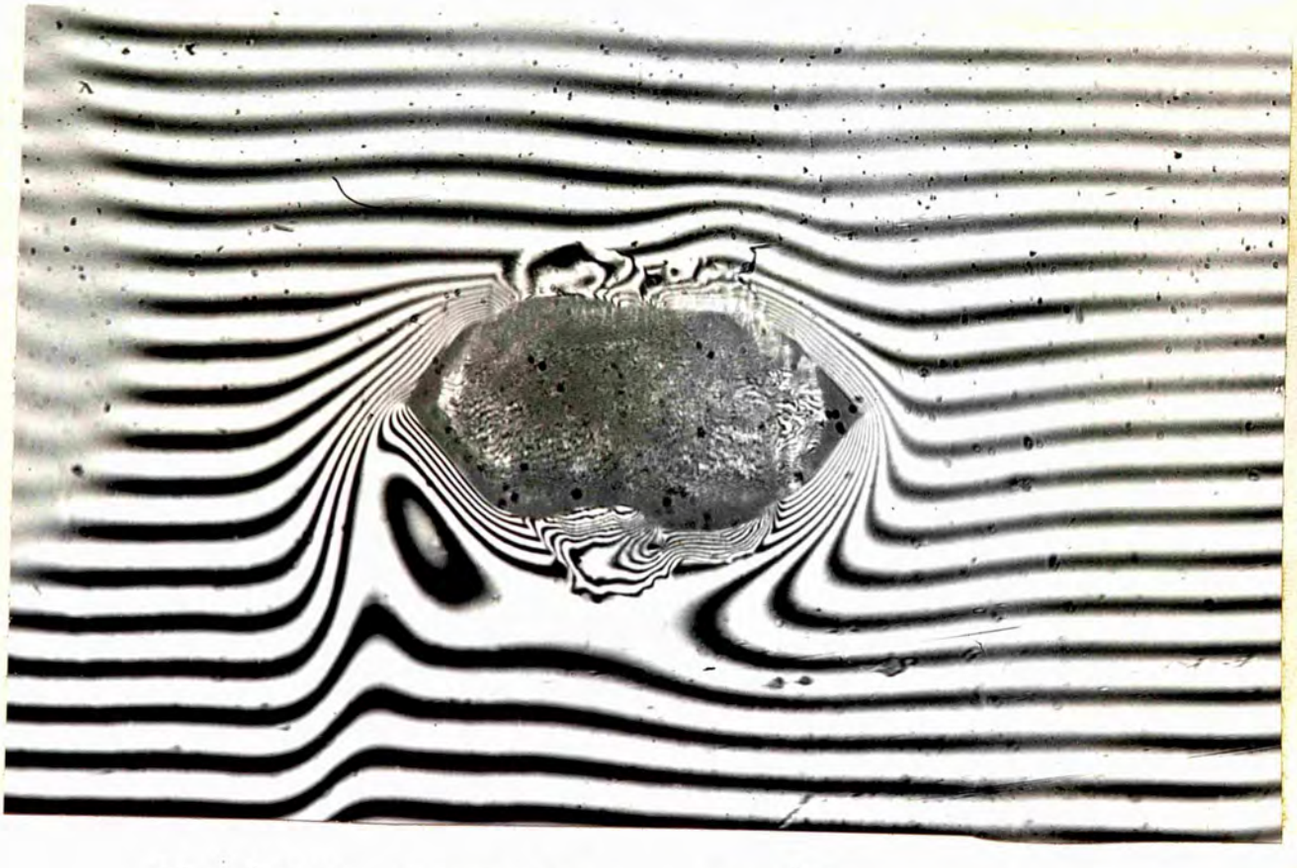


Fig. 6.4.2. Growth after Hrs. 45 Mins. x 19

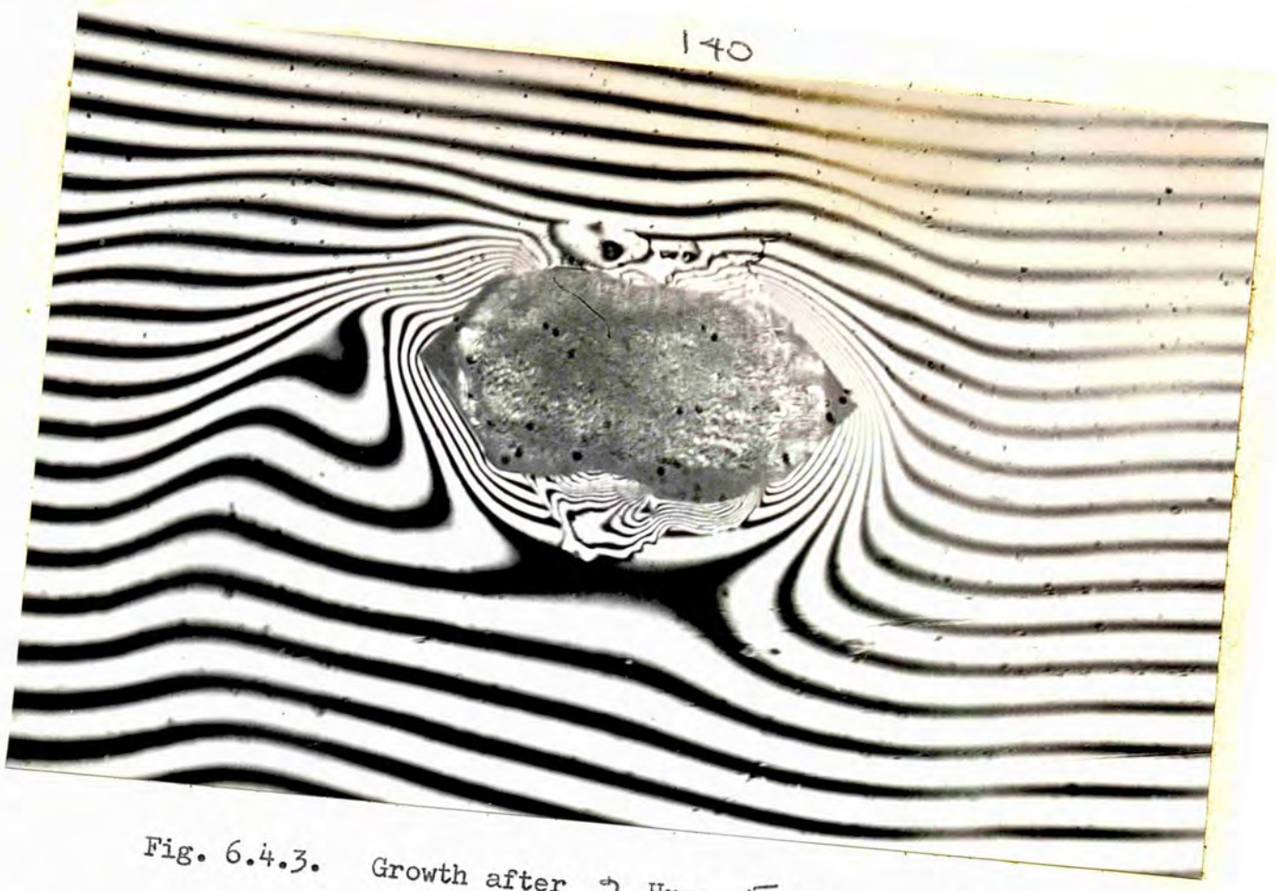


Fig. 6.4.3. Growth after 2 Hrs. 5 Mins. x 19

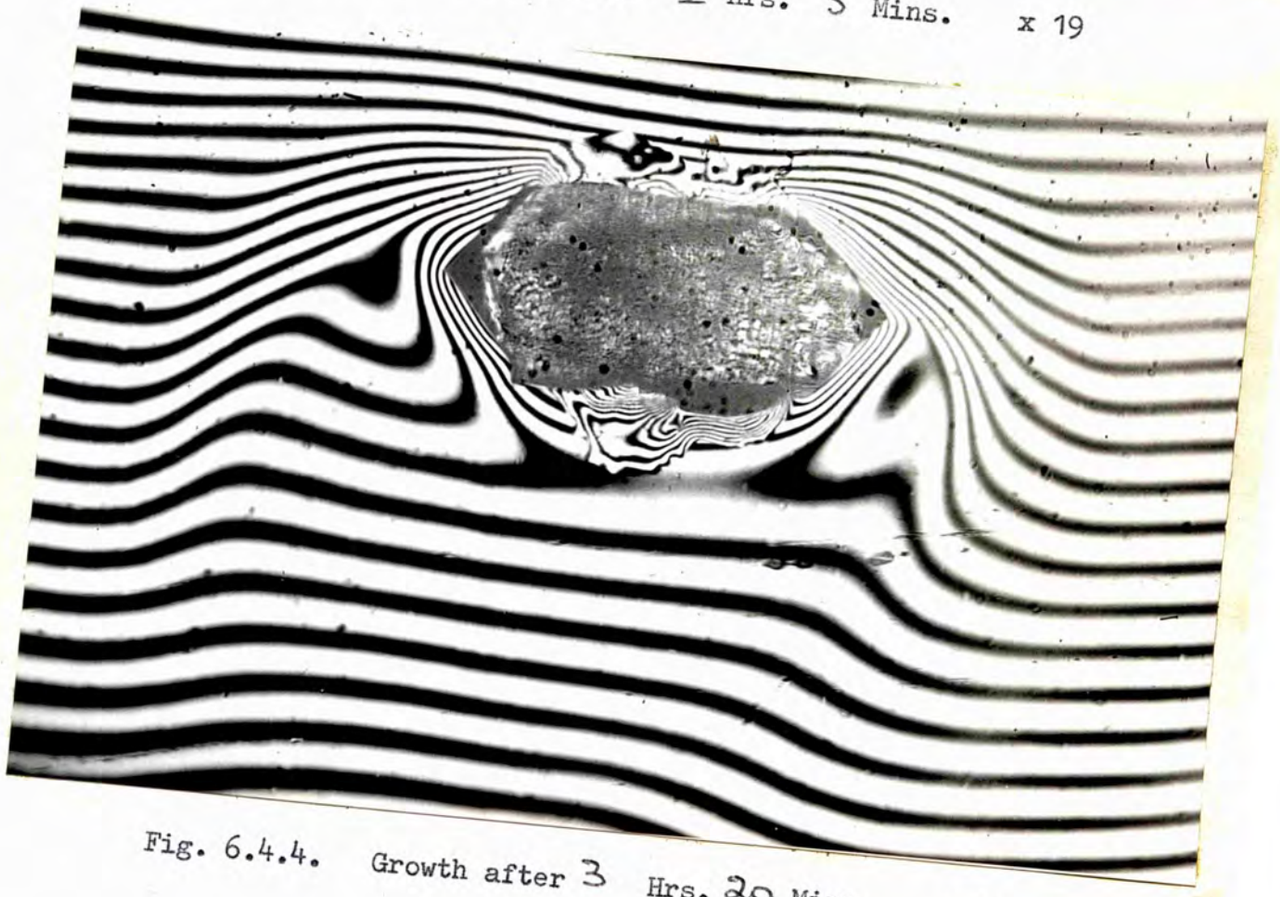


Fig. 6.4.4. Growth after 3 Hrs. 20 Mins. x 19

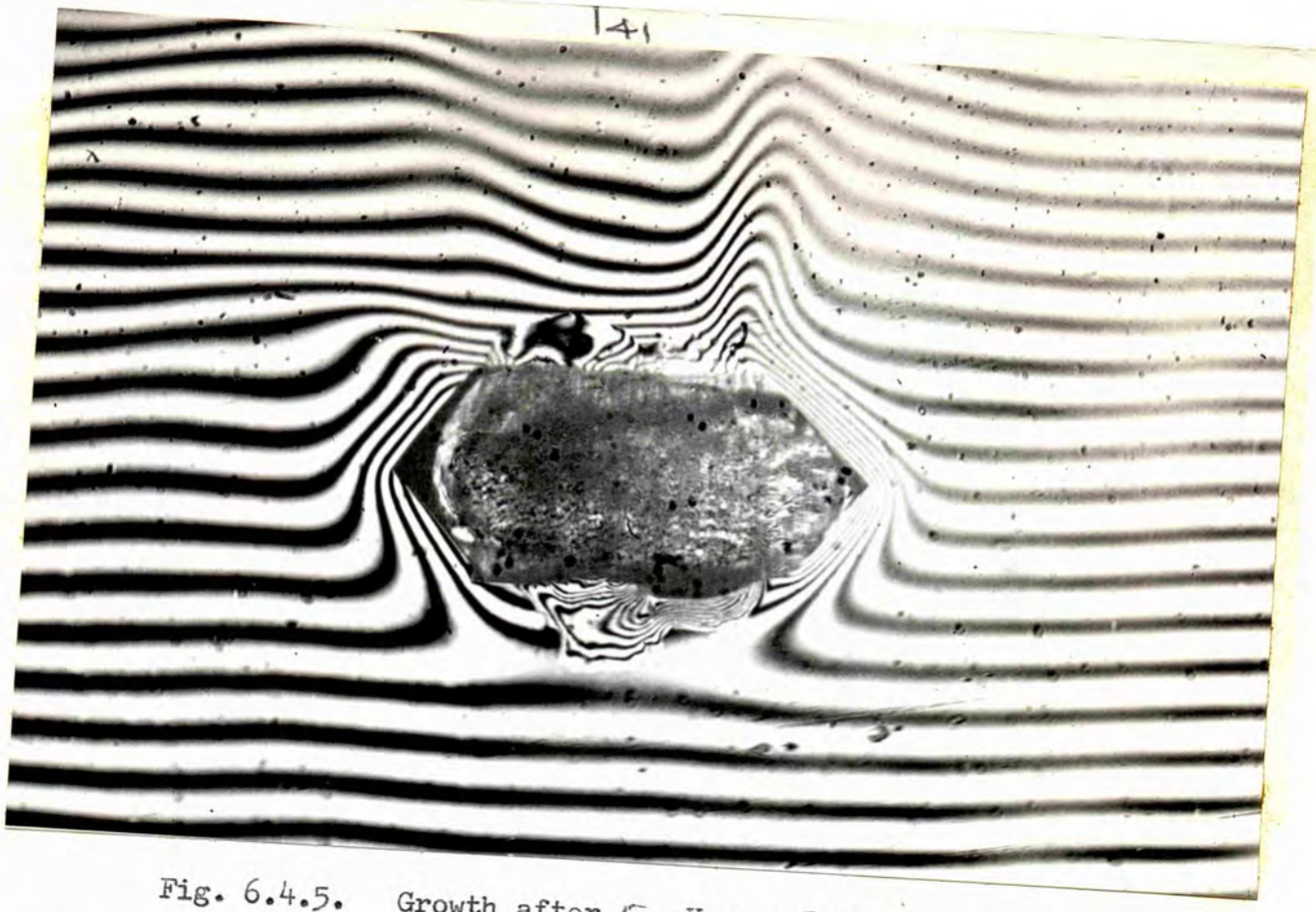


Fig. 6.4.5. Growth after 5 Hrs. 15 Mins. x 19

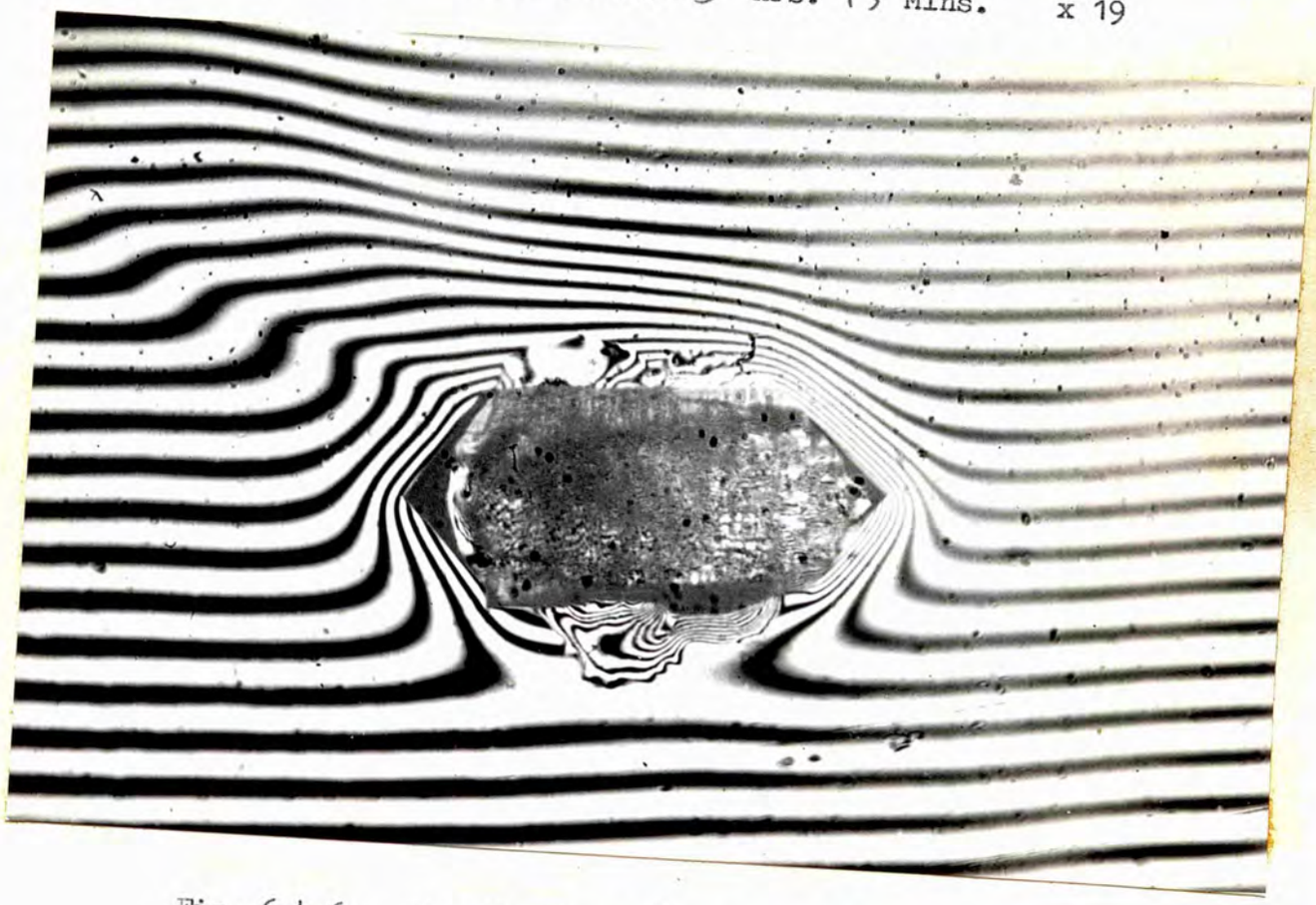


Fig. 6.4.6. Growth after 6 Hrs. 37 Mins. x 19

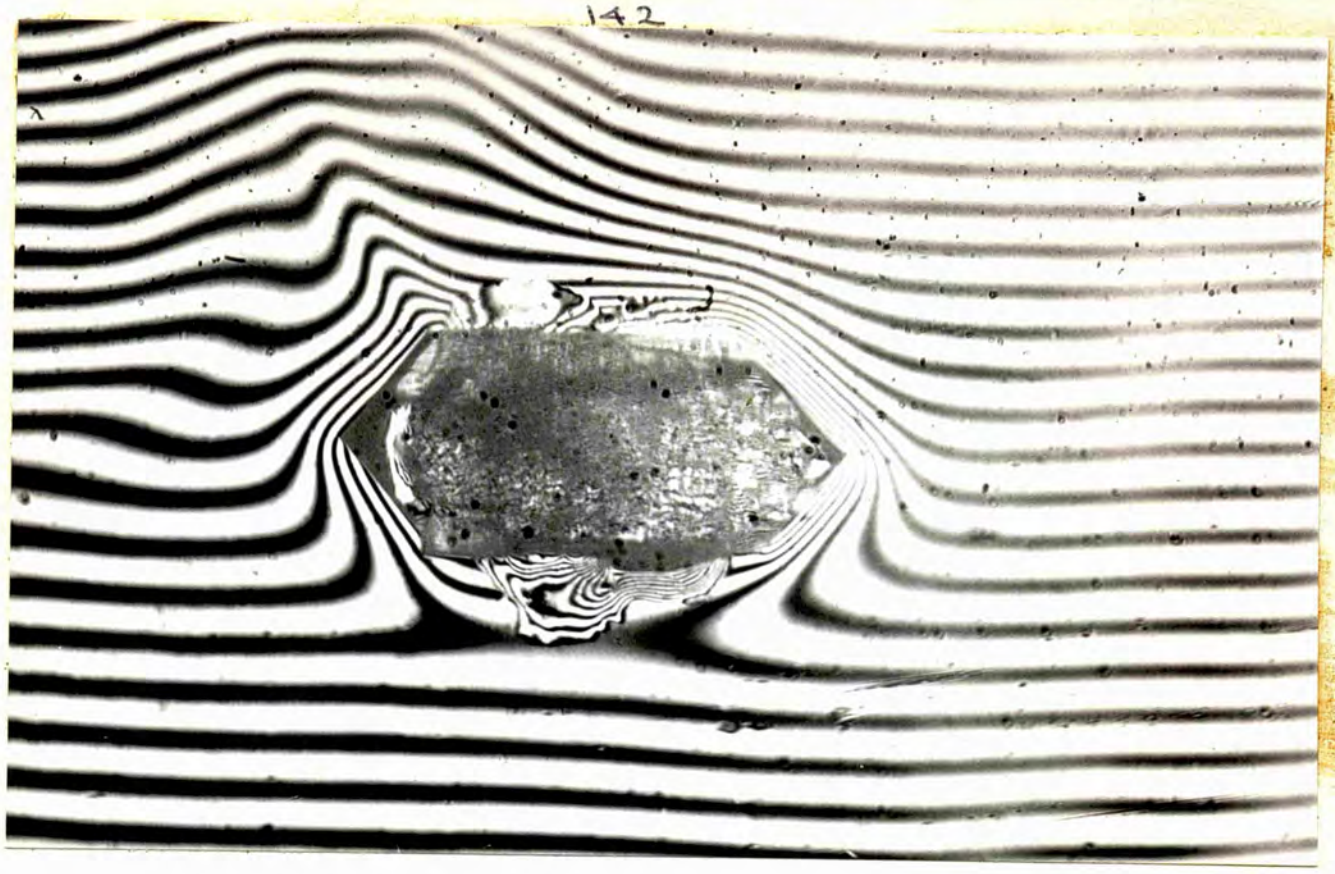


Fig. 6.4.7. Growth after 7 Hrs. 20 Mins. x 19

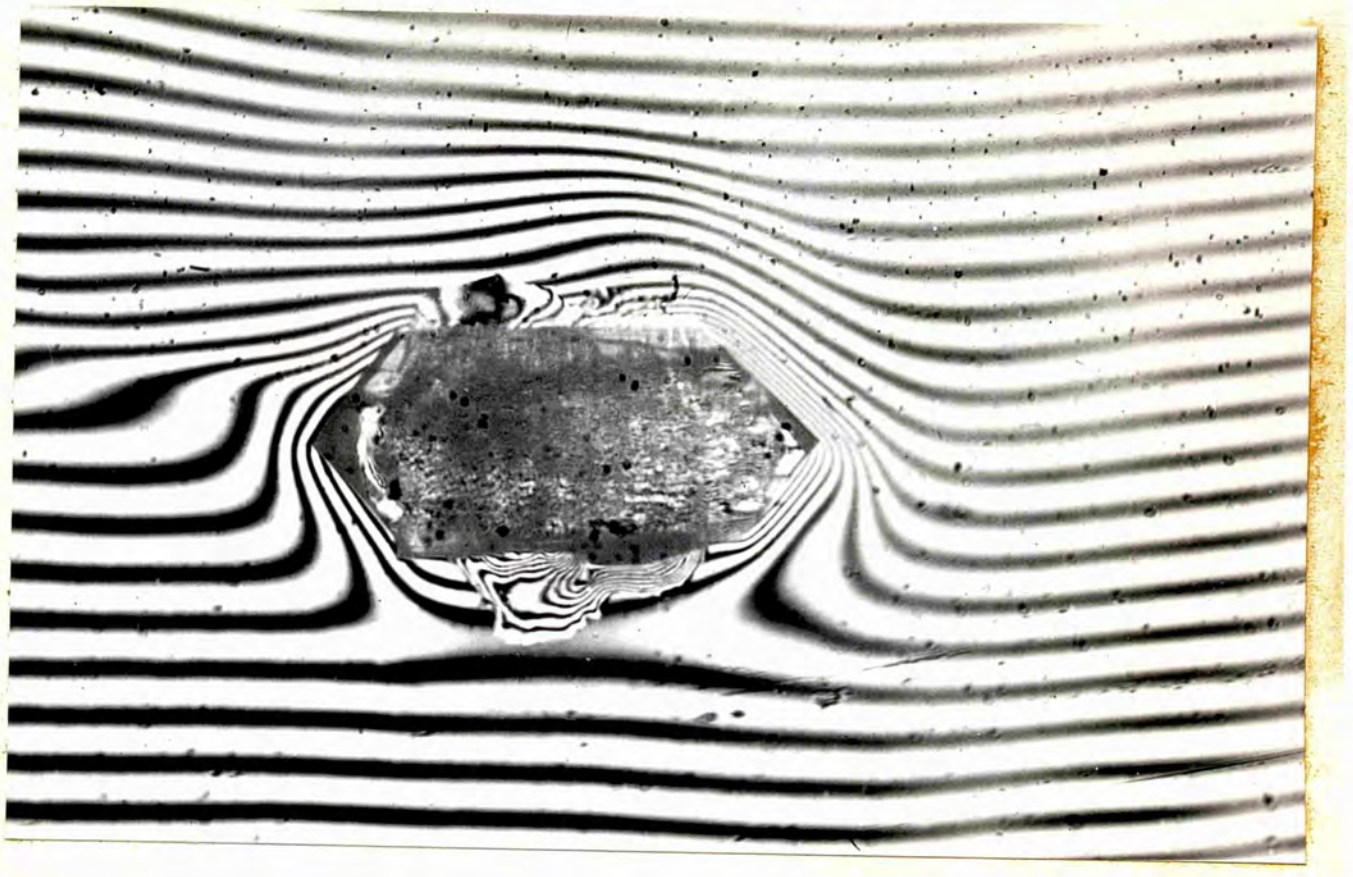


Fig. 6.4.8. Growth after 7 Hrs. 51 Mins. x 19

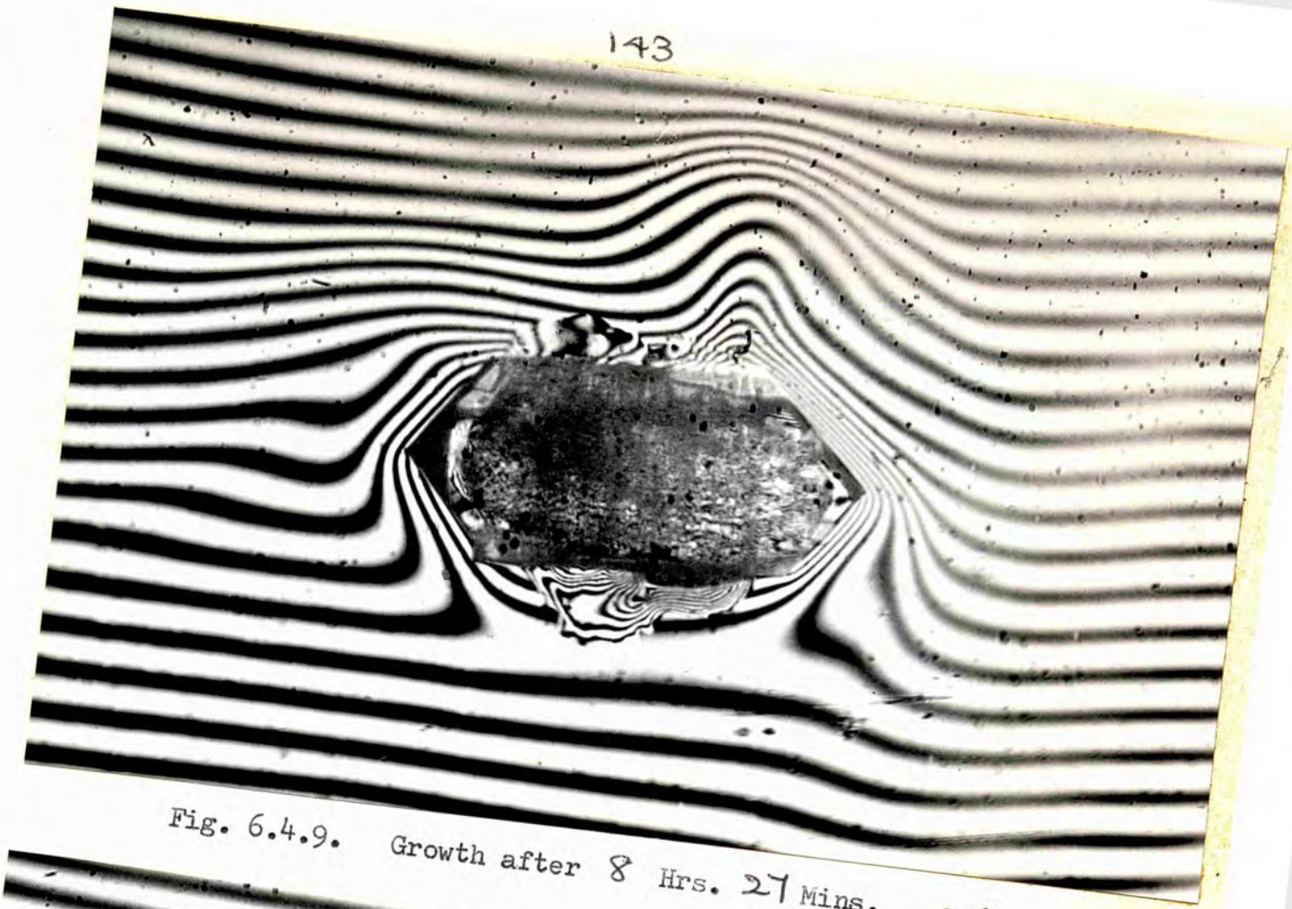


Fig. 6.4.9. Growth after 8 Hrs. 27 Mins. x 19

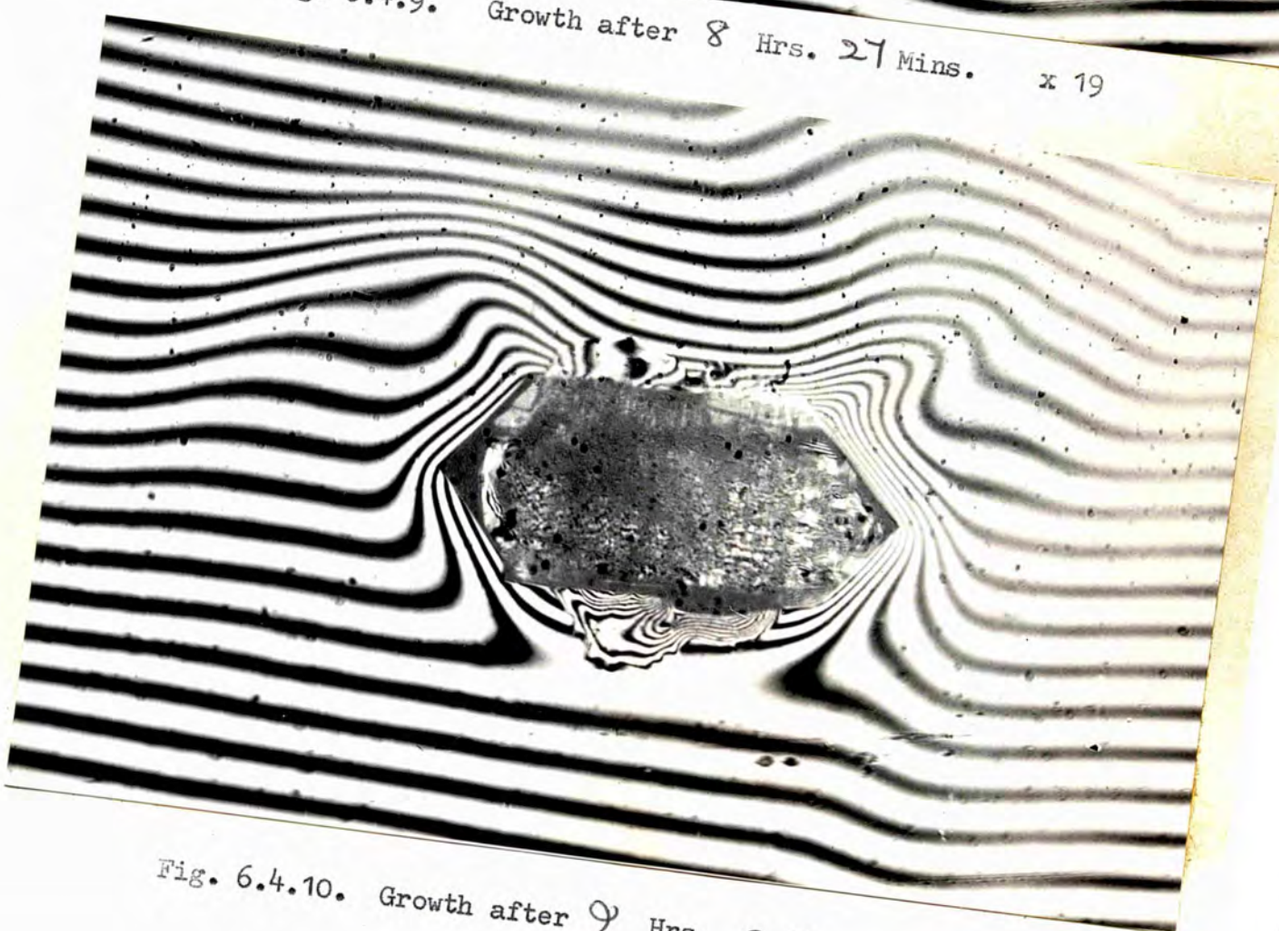


Fig. 6.4.10. Growth after 9 Hrs. 0 Mins. x 19

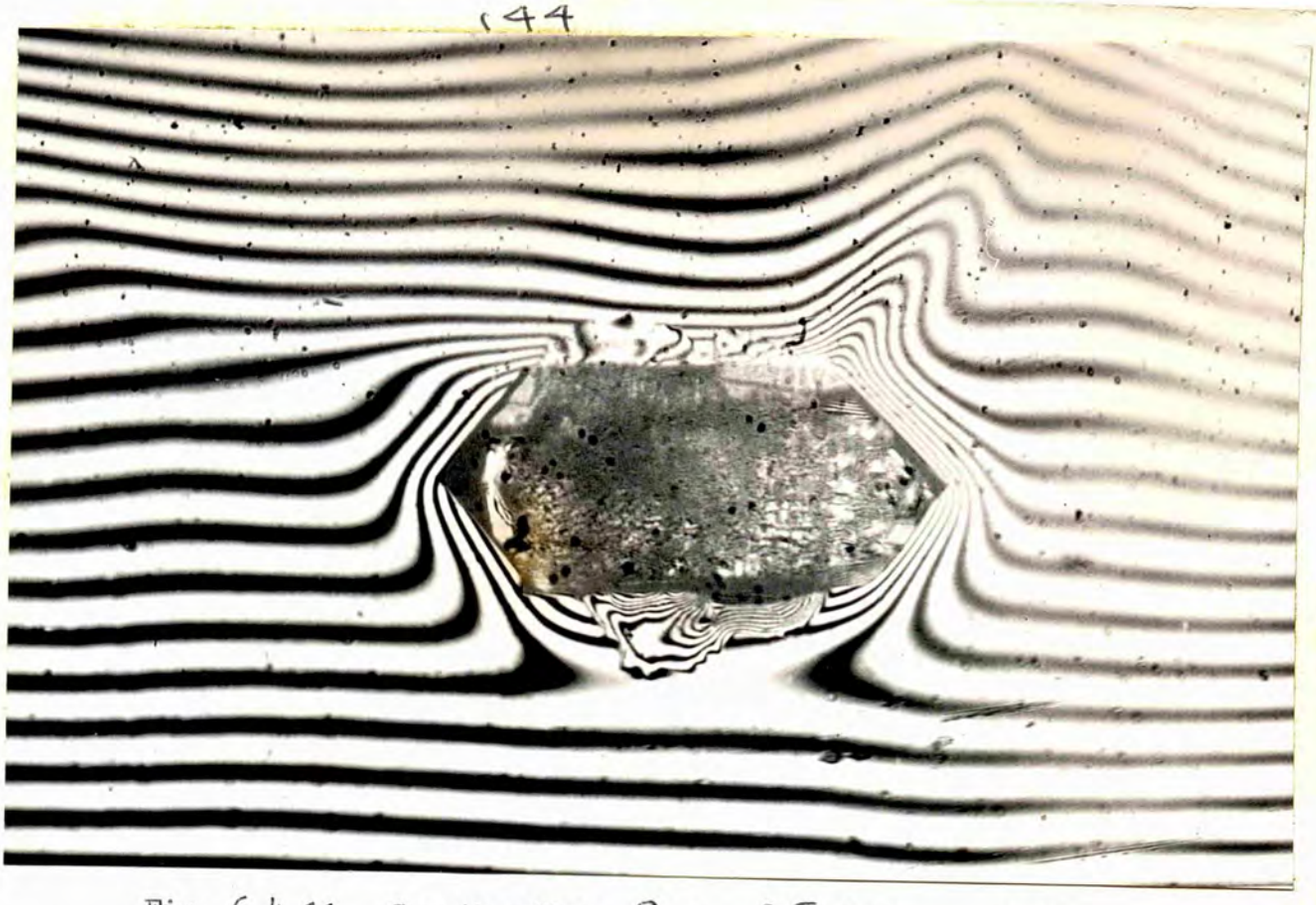


Fig. 6.4.11 Growth after 9 Hrs. 35 Mins. x 19

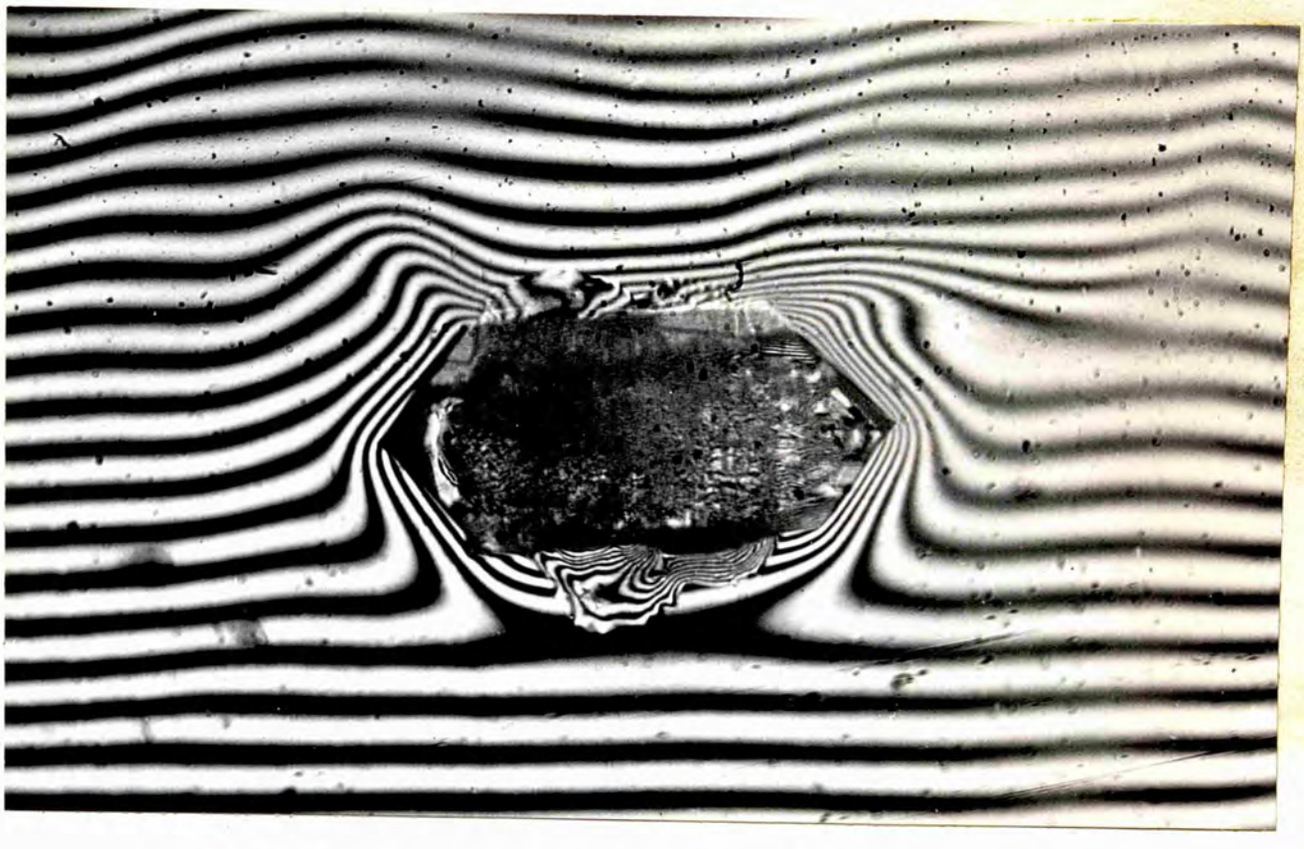


Fig. 6.4.12 Growth after 10 Hrs. 12 Mins. x 19

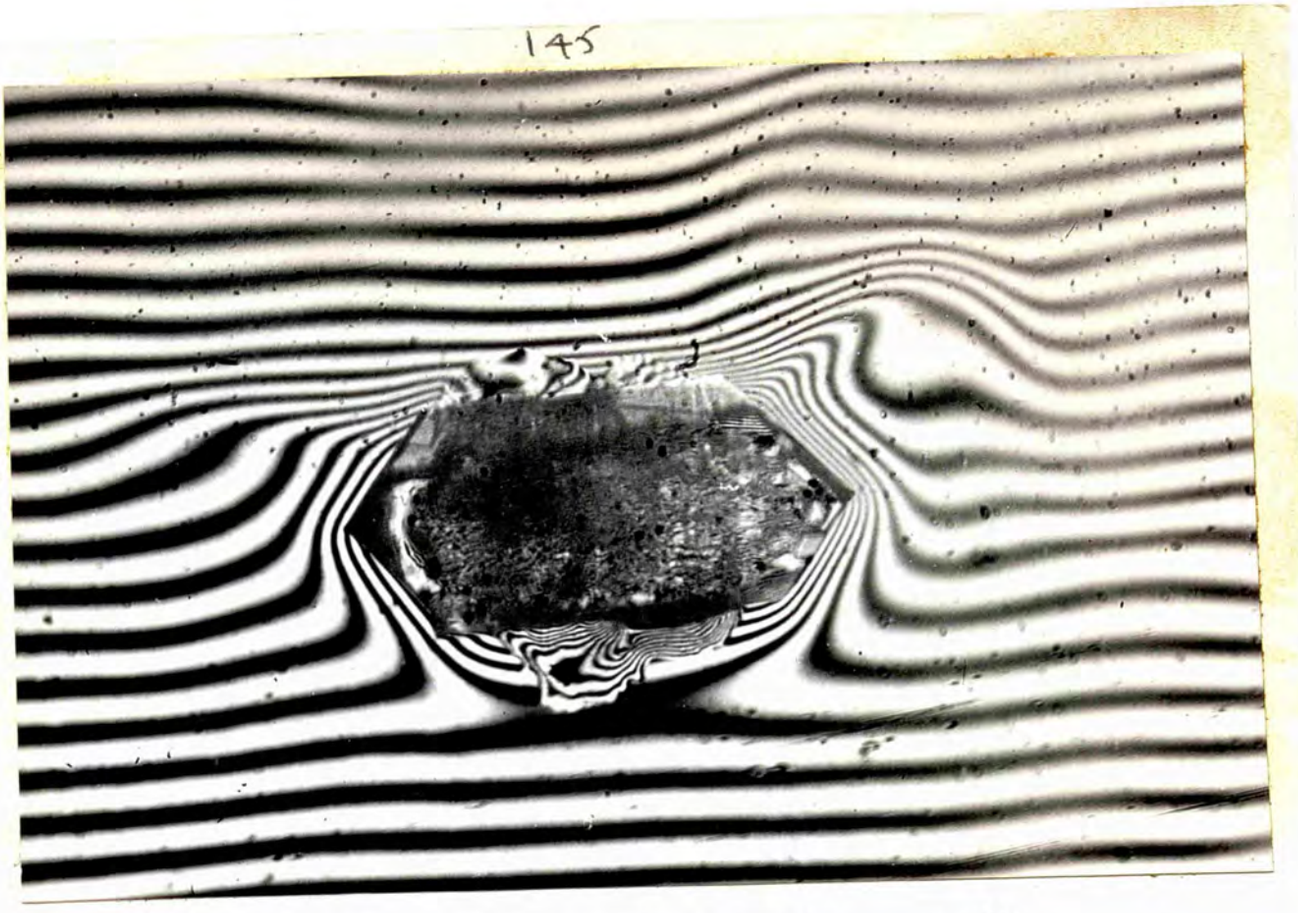


Fig. 6.4.13 Growth after 10 Hrs. 30 Mins x 19

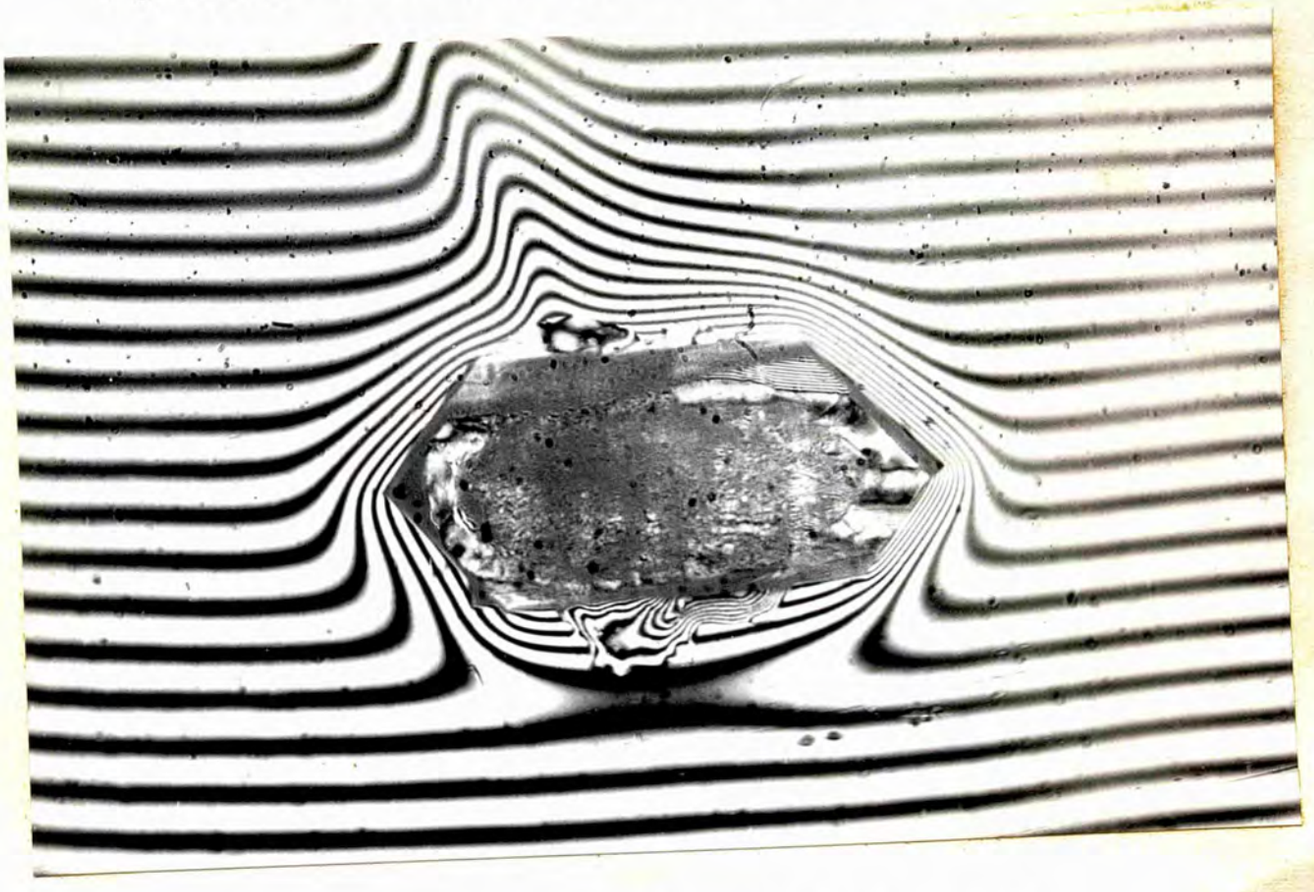


Fig. 6.4.14 Growth after 21 Hrs. 0 Mins. x 19

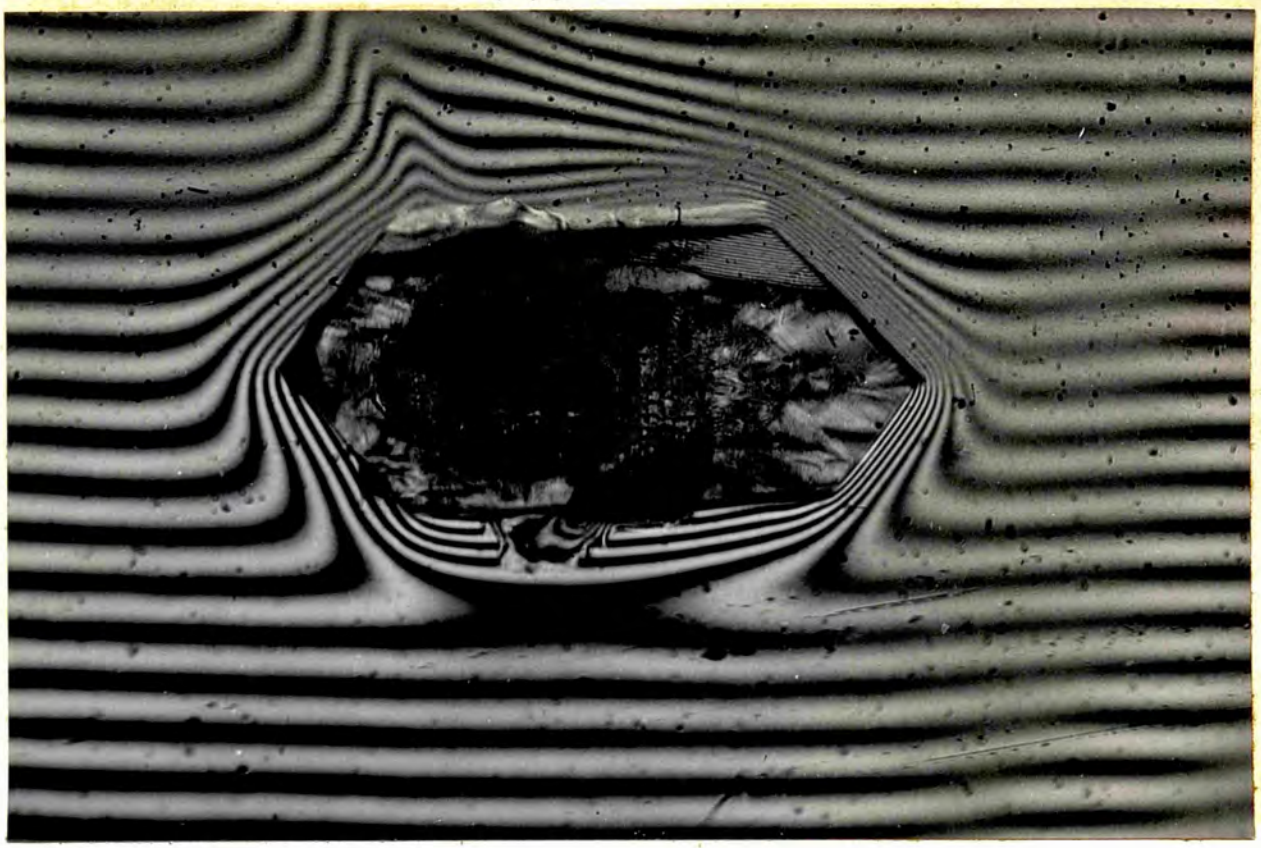


Fig. 6.4.15 Growth after 34 Hrs. 10 Mins. x 19

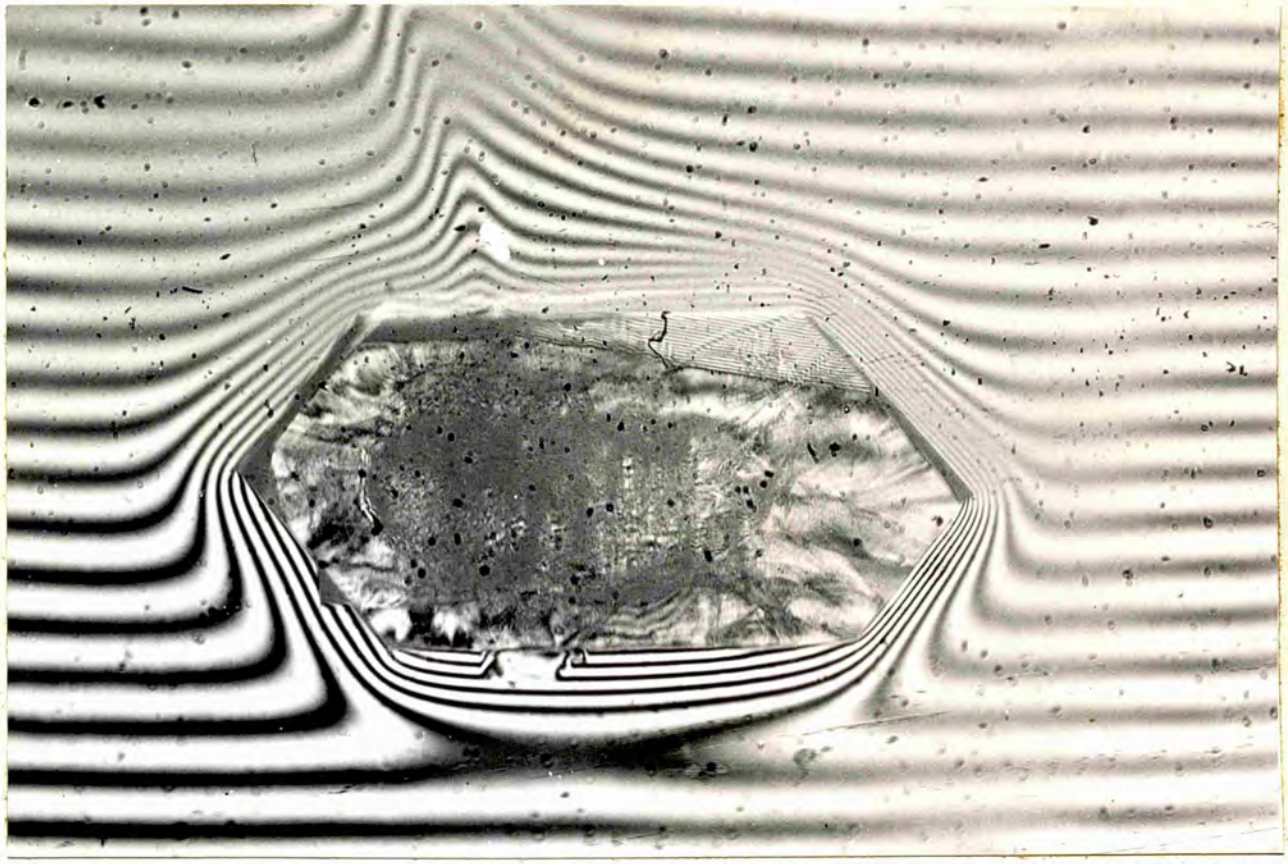


Fig. 6.4.16 Growth after 54 Hrs. 0 Mins. x 19

Crystal 4

The initial concentration of the solution was 71.2%.

In Fig. 6.4.1. can be seen the streaming effect due to dissolution with associated concentration gradients. The effect observed is very similar to that during the process of growth.

(The pattern at the upper and lower faces of the crystal is due to the fact that during the mounting process some adhesive has spread beyond the edges of the crystal. This unfortunately prevents any calculation of the concentration along these faces).

With solutions of such low concentration the streaming effect was found to take some time to become established and in this case there is a great deal of disturbance in the solution before it actually succeeds. The first indications of an upward movement in the solution can be seen on the left hand side of the crystal in Fig. 6.4.3. At a time of 3 hours 20 mins. there is a similar effect at the right hand faces. This has resulted in a stream in Fig. 6.4.5. and measurements show that the concentration the faces BC and CD has risen from a value of 70% to 70.3%. This stream had disappeared by the time the next photograph was taken but the concentration at the face has not changed significantly, presumably because the crystal has such a slow rate of growth. There are indications of a not very well pronounced stream from the face FA. This is more marked in Fig. 6.4.7 and the concentra-

tion along these faces has increased from a value of approximately 70.5% to 70.7%. There are disturbances in Fig. 6.4.8 but no distinct sign of streaming.

The effect of streaming continually comes and goes throughout the process of growth but there are no appreciable changes of concentration that can be measured, the value along the faces BC and CD is 70.3 ± 0.1% and this is maintained throughout the period of growth observed.

In this case the streaming does not appear to move along a face but becomes extinct at one corner and then reappears at the other. Also the effect in this case seems to cause a much more widespread disturbance throughout the area seen in the photographs, whereas for more concentration solutions it was mostly confined to a small region round the crystal.

On looking at the final photograph the outline of the original crystal can be seen and it is evident that once again the faces with the steeper gradient and lower value of concentration adjacent to them BC and CD has grown out to the greatest extent. This would appear to have occurred during the last 33 hours of growth as in Fig. 6.4.14. the crystal appears to have extended all its original faces by approximately the same amount. The planimeter was used to estimate the increase in surface area with time, but as the crystal did not grow at a very fast rate, any increase in

area was of the same order of magnitude as the error in measurement and therefore no suitable results could be obtained.

TABLE 6.4.

t = 0.164 cms.
μ_o = 1.4681

Change in fringe order Δn	Change in refractive index $\Delta\mu$	Refractive index at the face μ	Concentration at the face
3	0.0010	1.4671	70.8%
4	0.0013	1.4668	70.7%
5	0.0017	1.4664	70.52(5)%
6	0.0020	1.4661	70.4%
7	0.0023	1.4658	70.3%
8	0.0026	1.4655	70.22(5)%
9	0.0030	1.4651	70.0%
10	0.0033	1.4648	69.82(5)%
11	0.0036	1.4645	69.75%

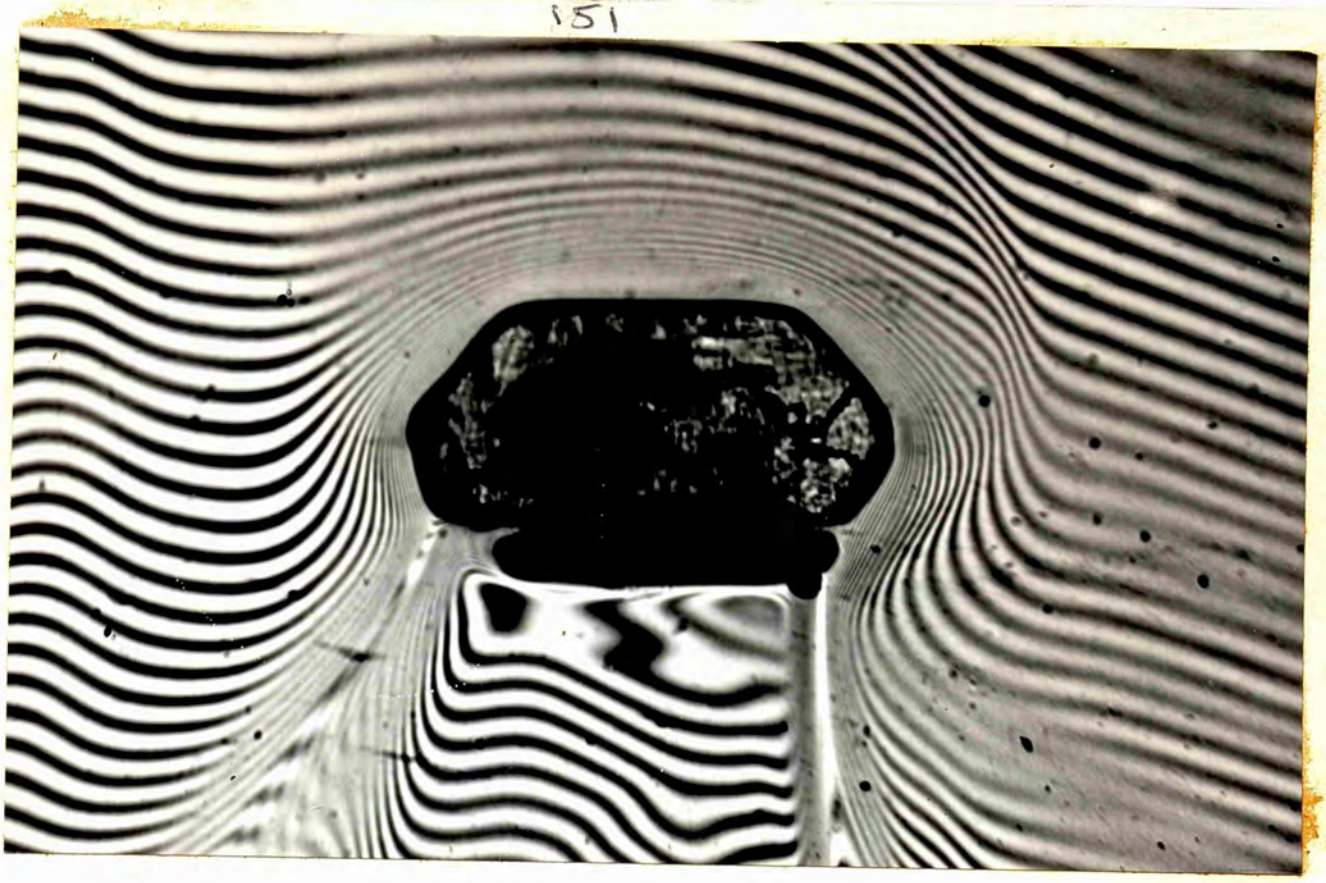


Fig. 6.5.1. Growth after Hrs. 7 Mins. x 20

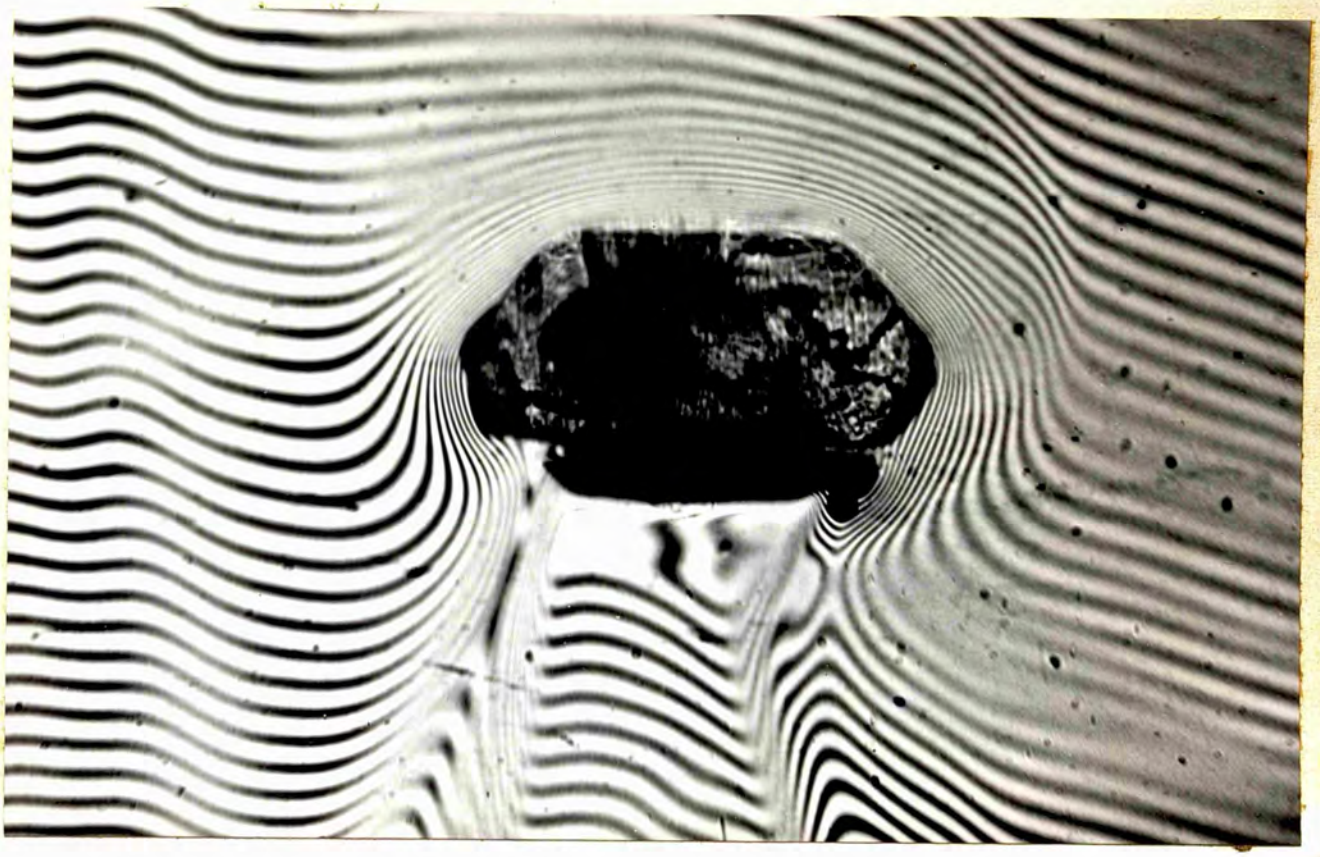


Fig. 6.5.2. Growth after Hrs. 9 Mins. x 20

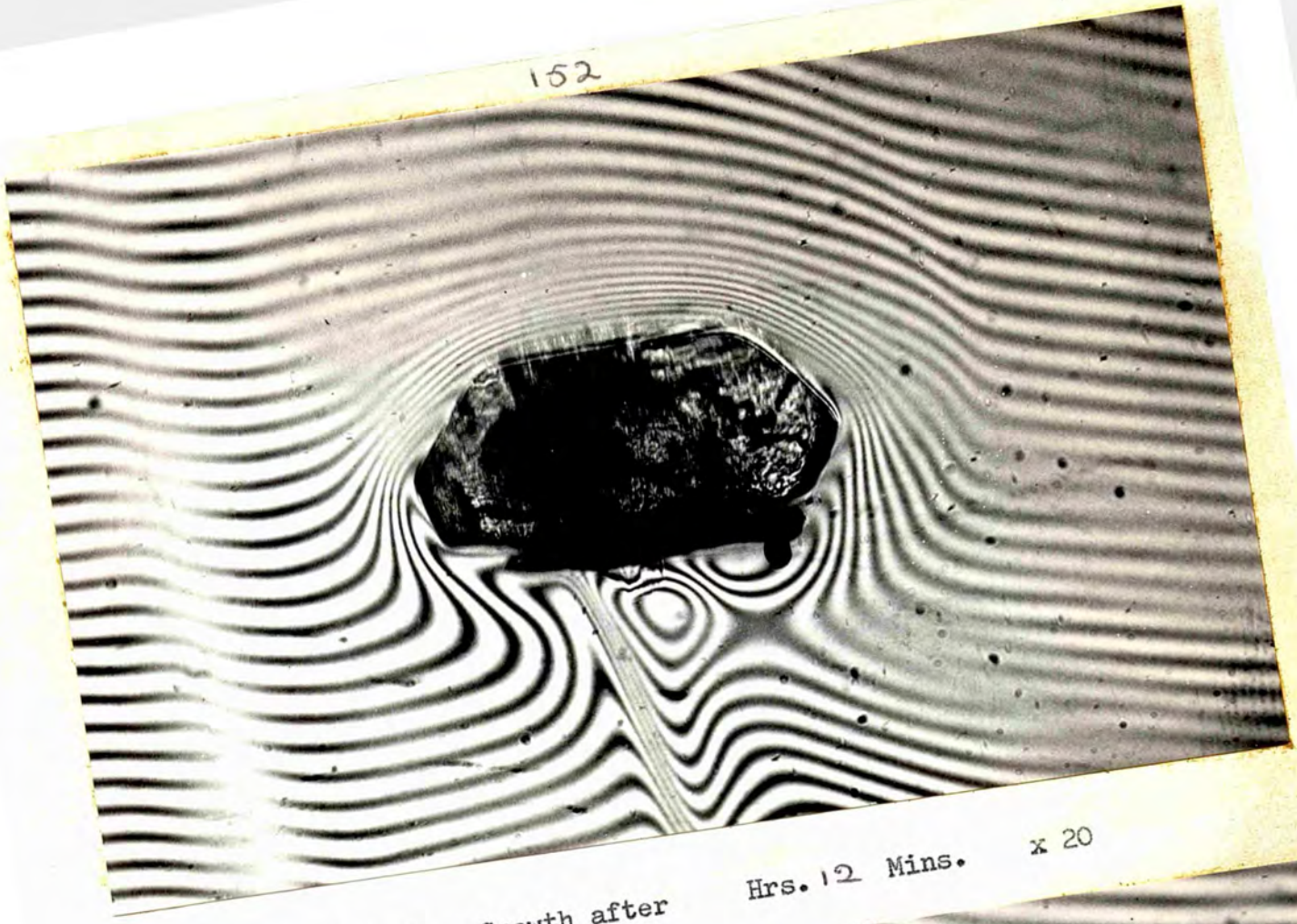


Fig. 6.5.3. Growth after Hrs. 12 Mins. x 20

Fig. 6.5.4. Growth after Hrs. 14 Mins. x 20

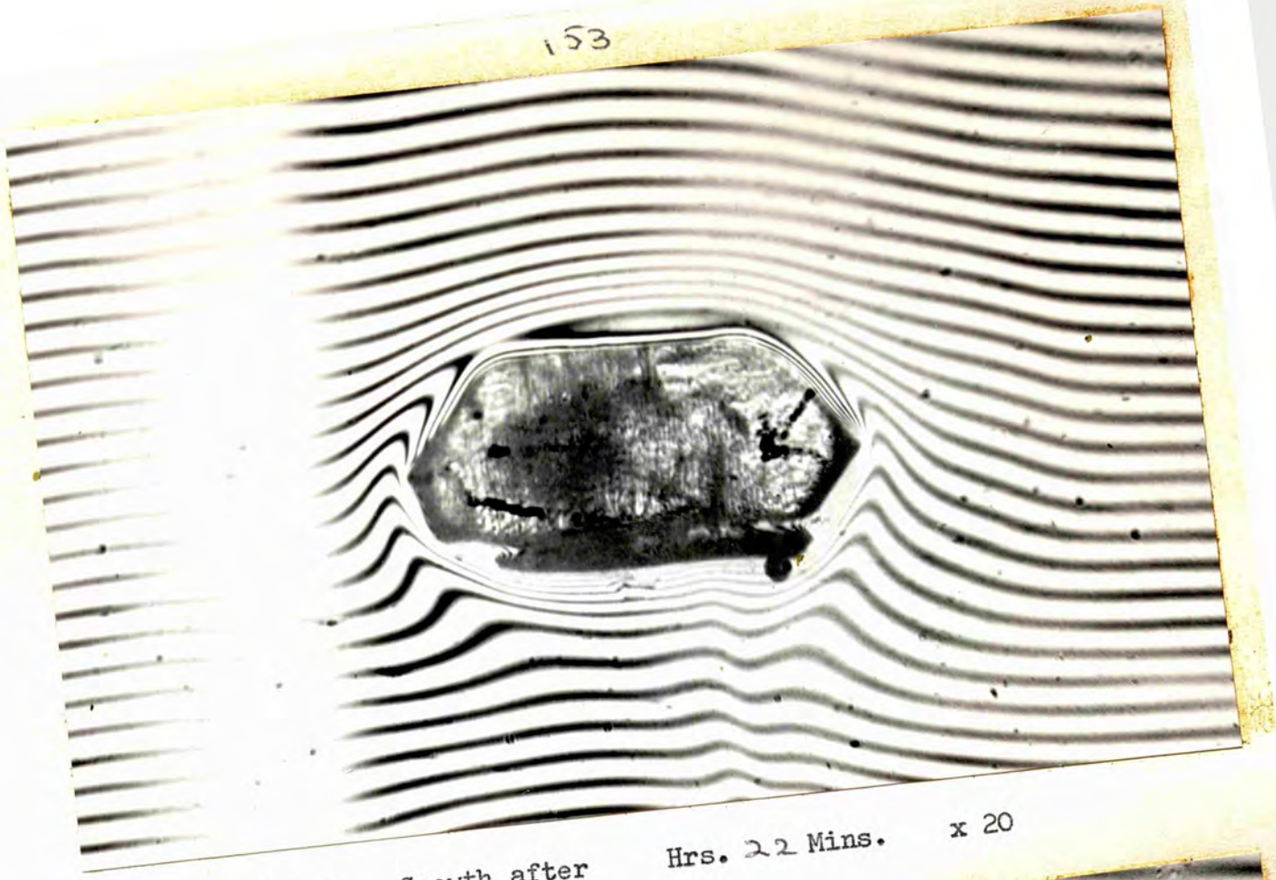


Fig. 6.5.5. Growth after Hrs. 22 Mins. x 20

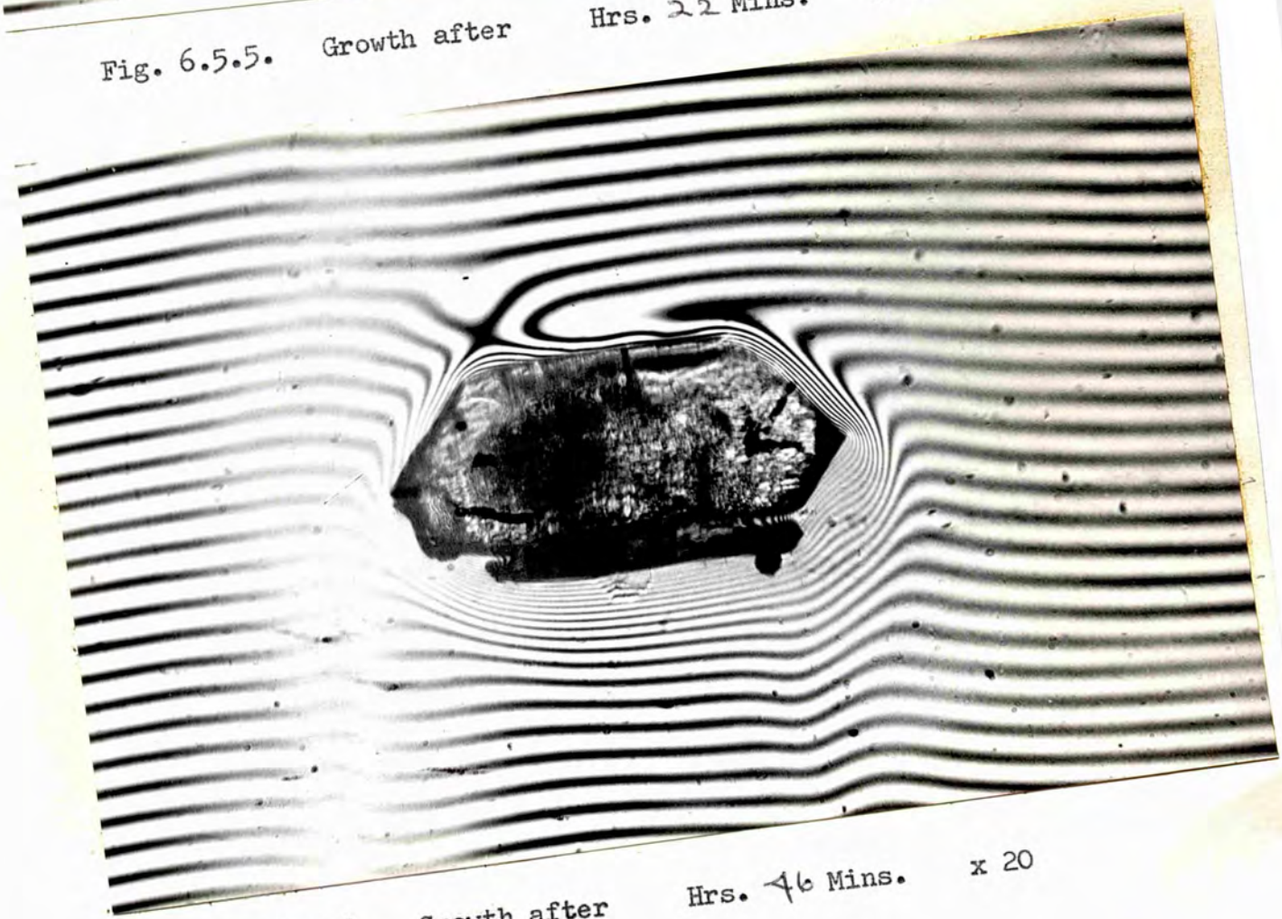


Fig. 6.5.6. Growth after Hrs. 46 Mins. x 20

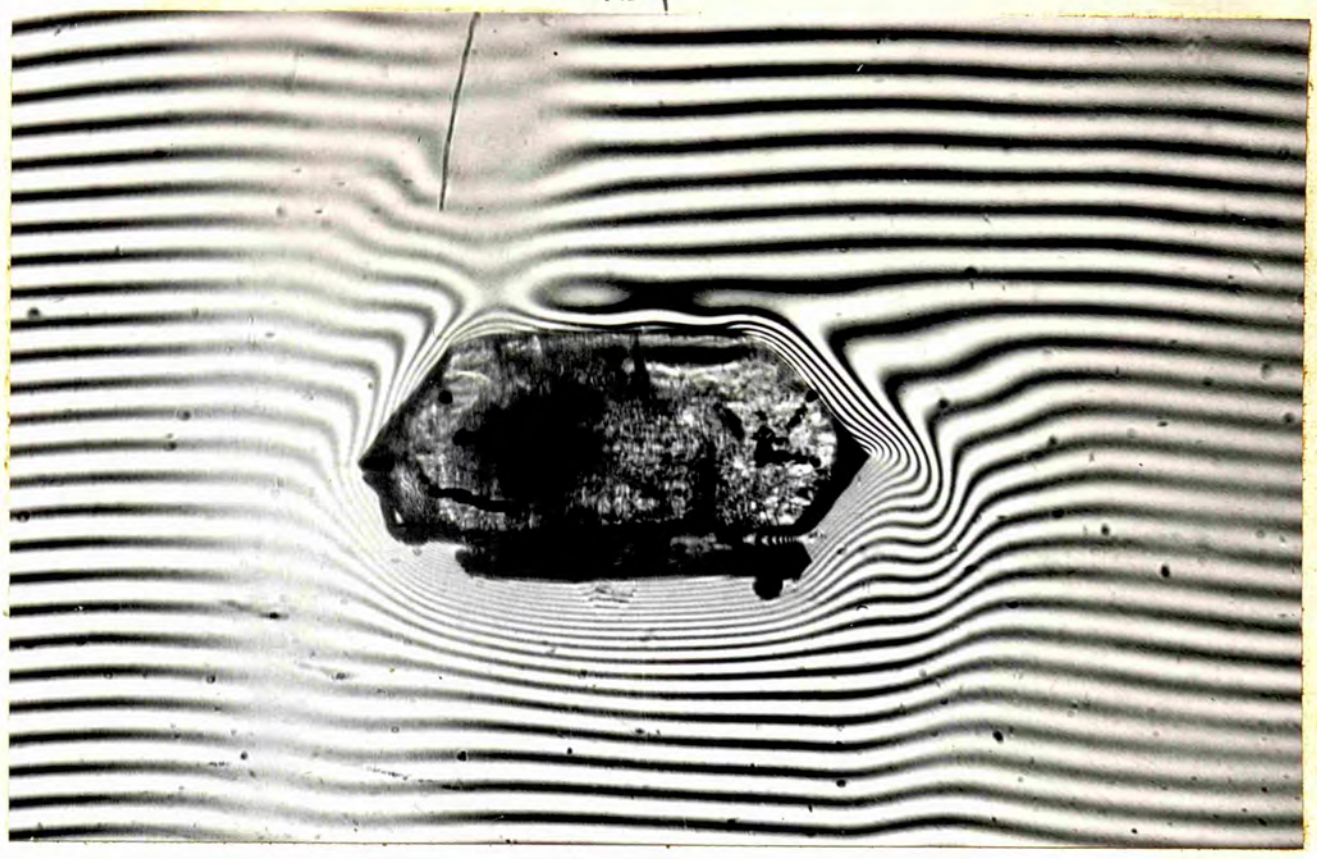


Fig. 6.5.7. Growth after 1 Hrs. Mins. x 20

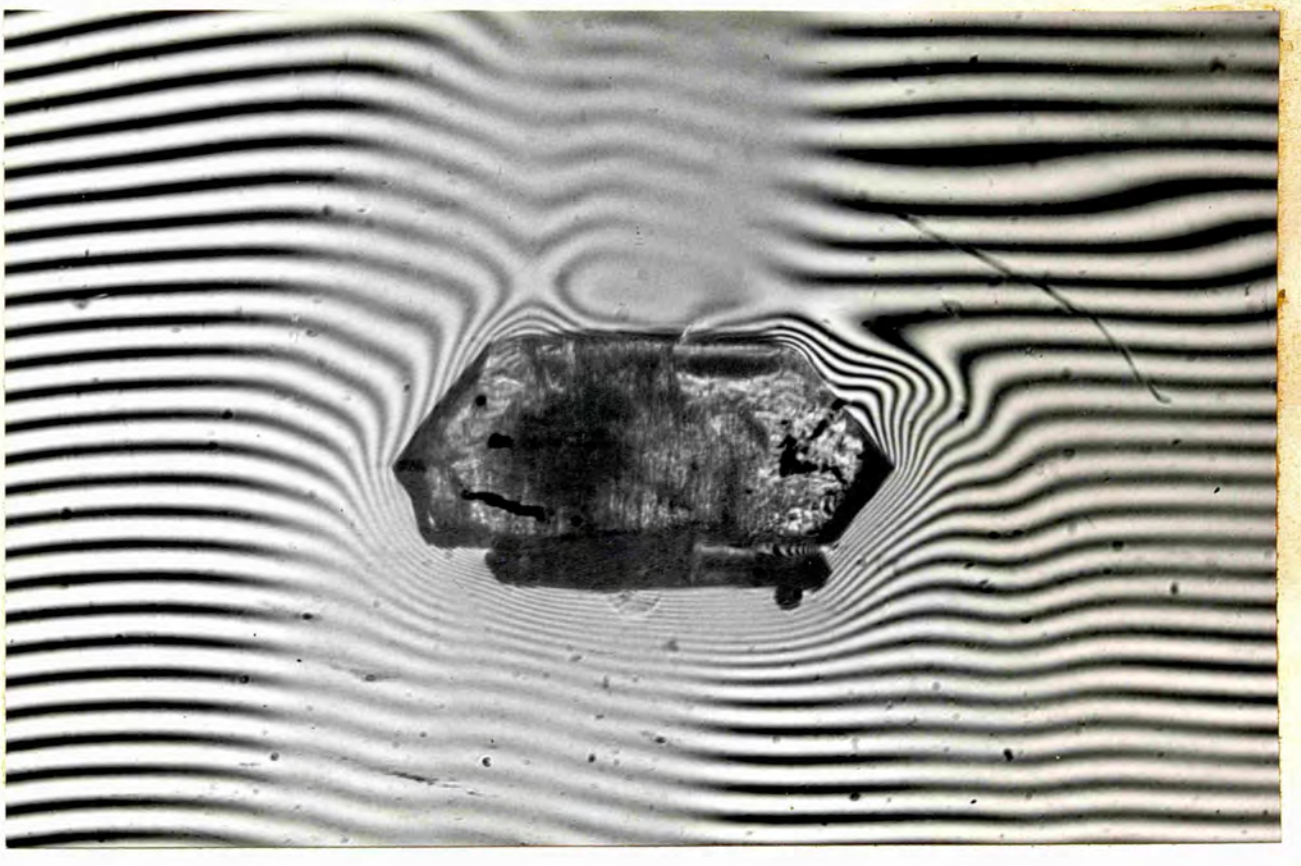


Fig. 6.5.8. Growth after 1 Hrs. 32 Mins. x 20

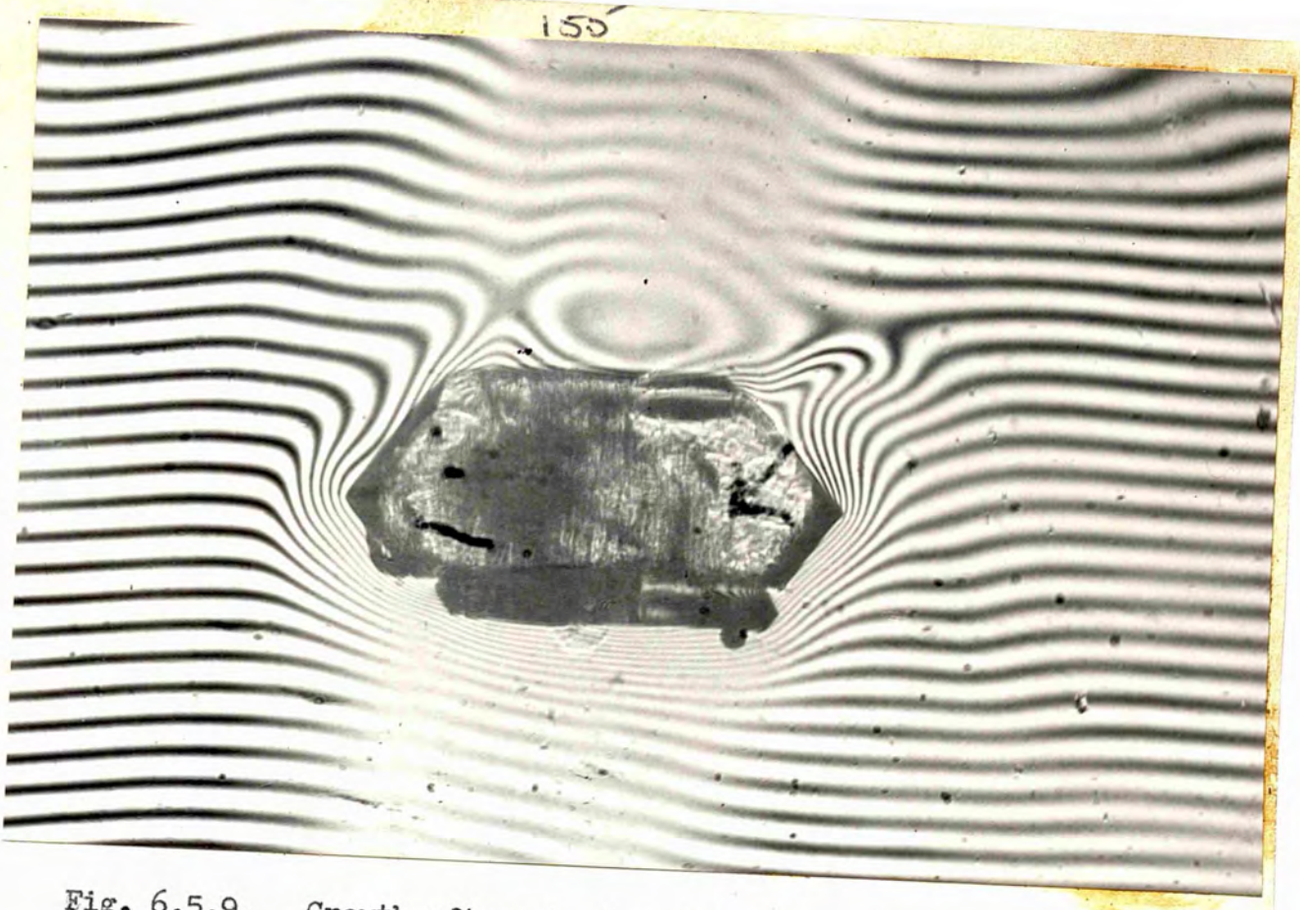


Fig. 6.5.9. Growth after 1 Hrs. 53 Mins. x 20

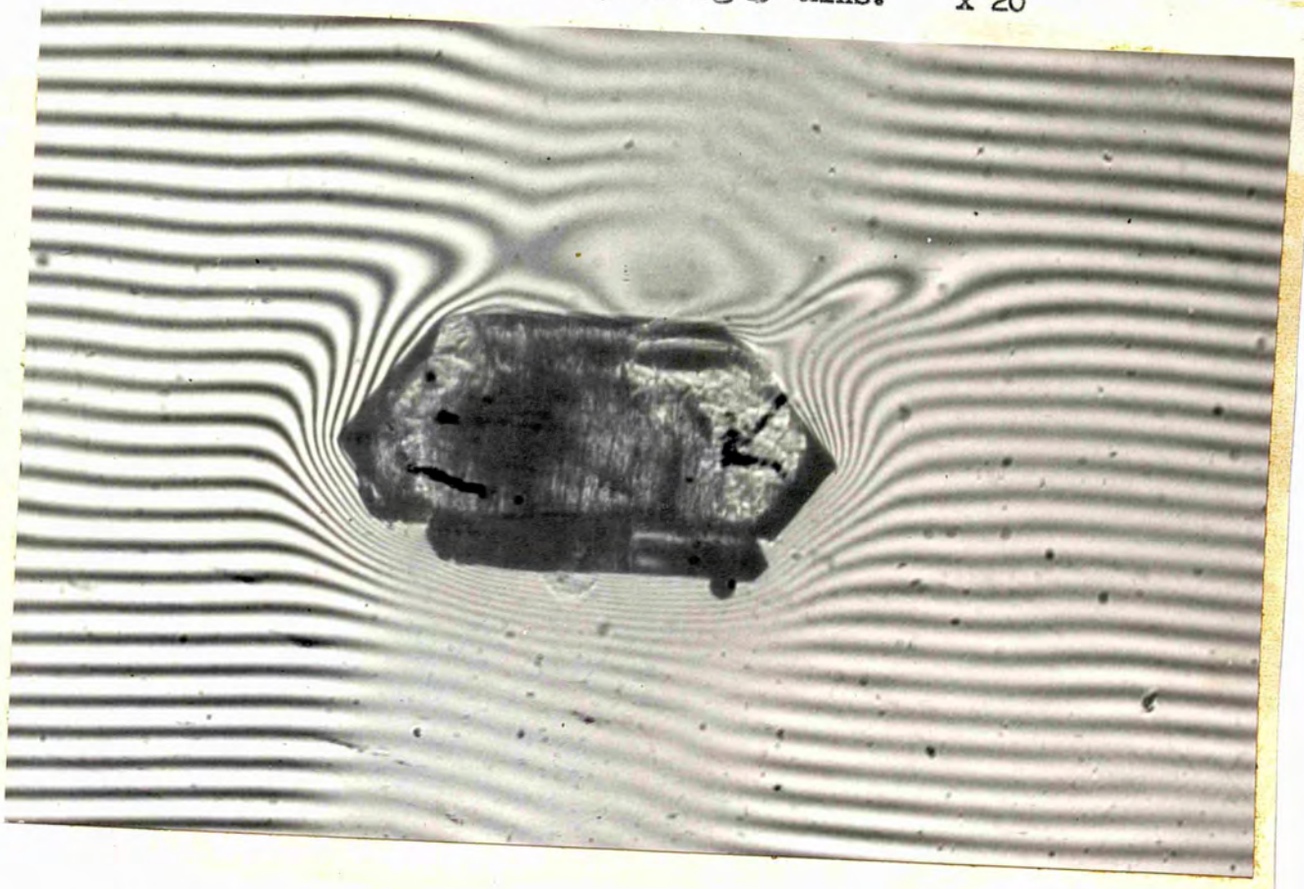


Fig. 6.5.10. Growth after 2 Hrs. 6 Mins. x 20

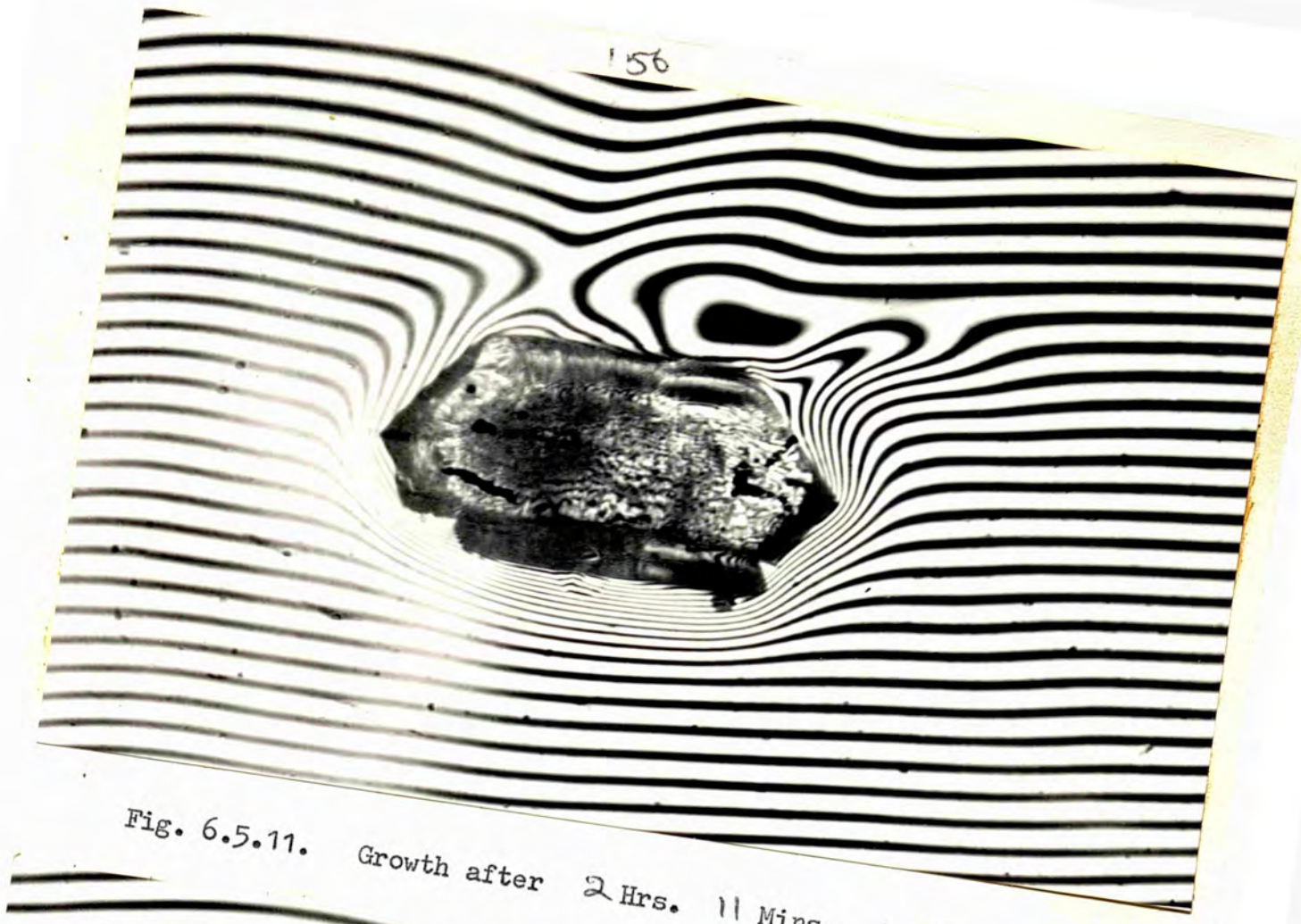


Fig. 6.5.11. Growth after 2 Hrs. 11 Mins. x 20

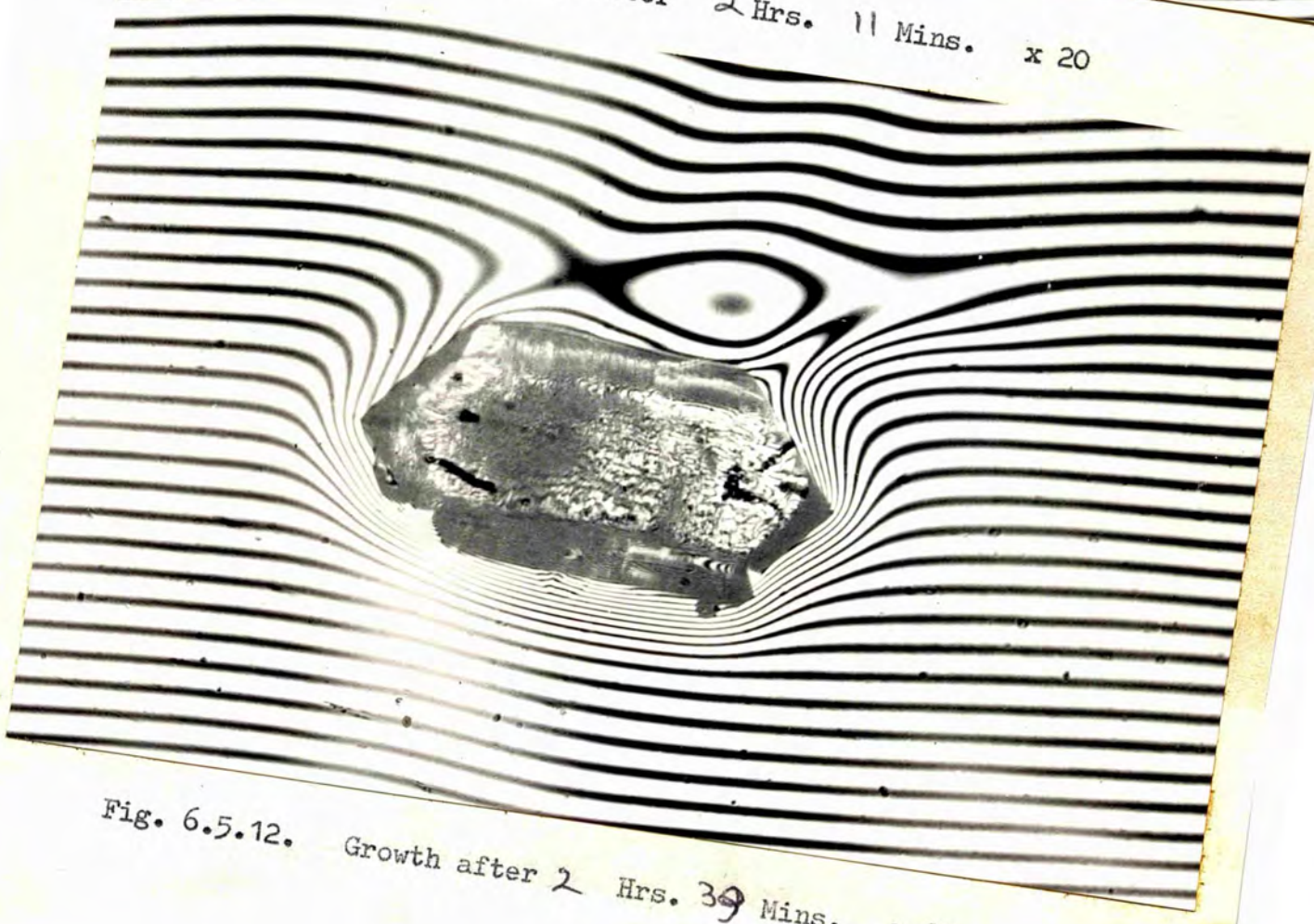


Fig. 6.5.12. Growth after 2 Hrs. 39 Mins. x 20

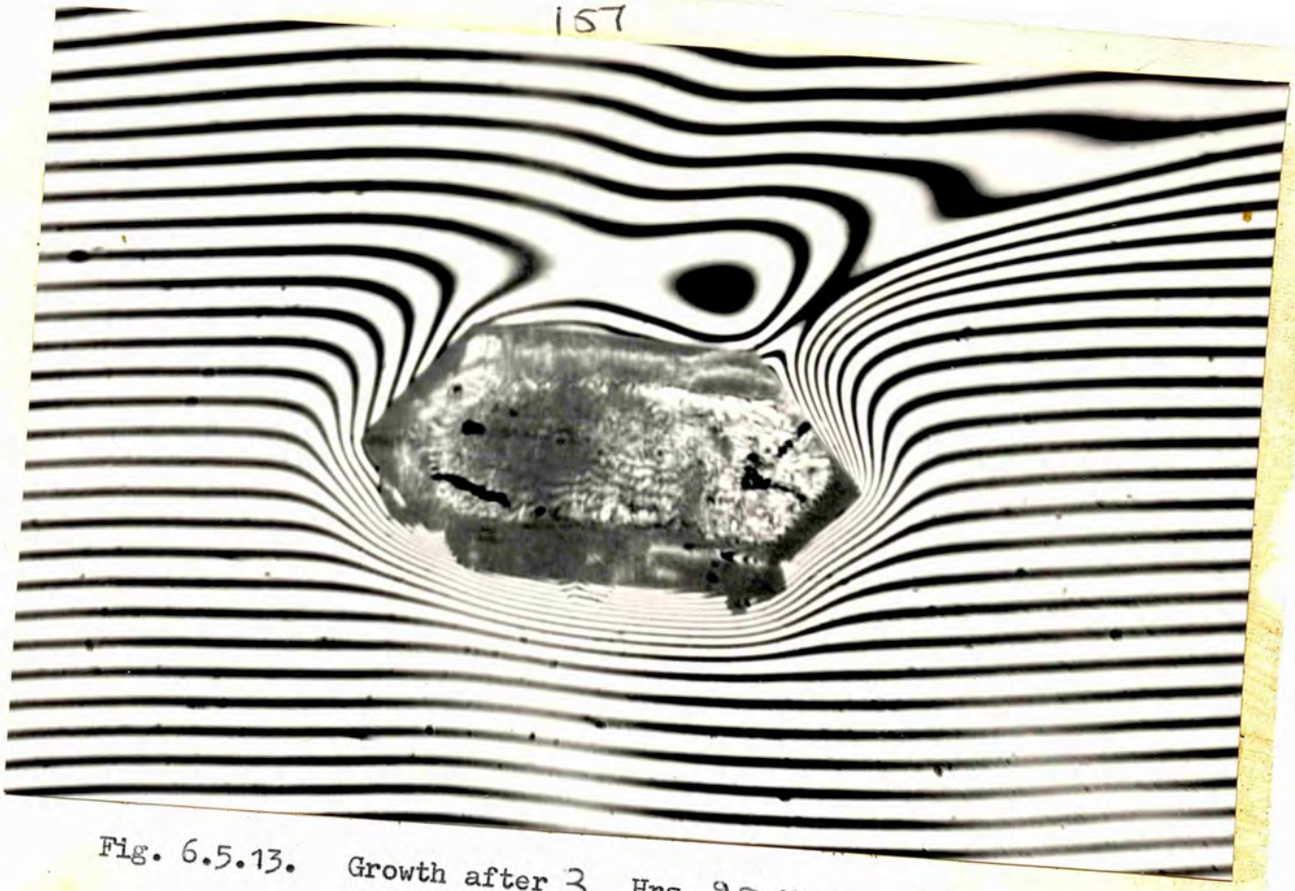


Fig. 6.5.13. Growth after 3 Hrs. 20 Mins. x 20

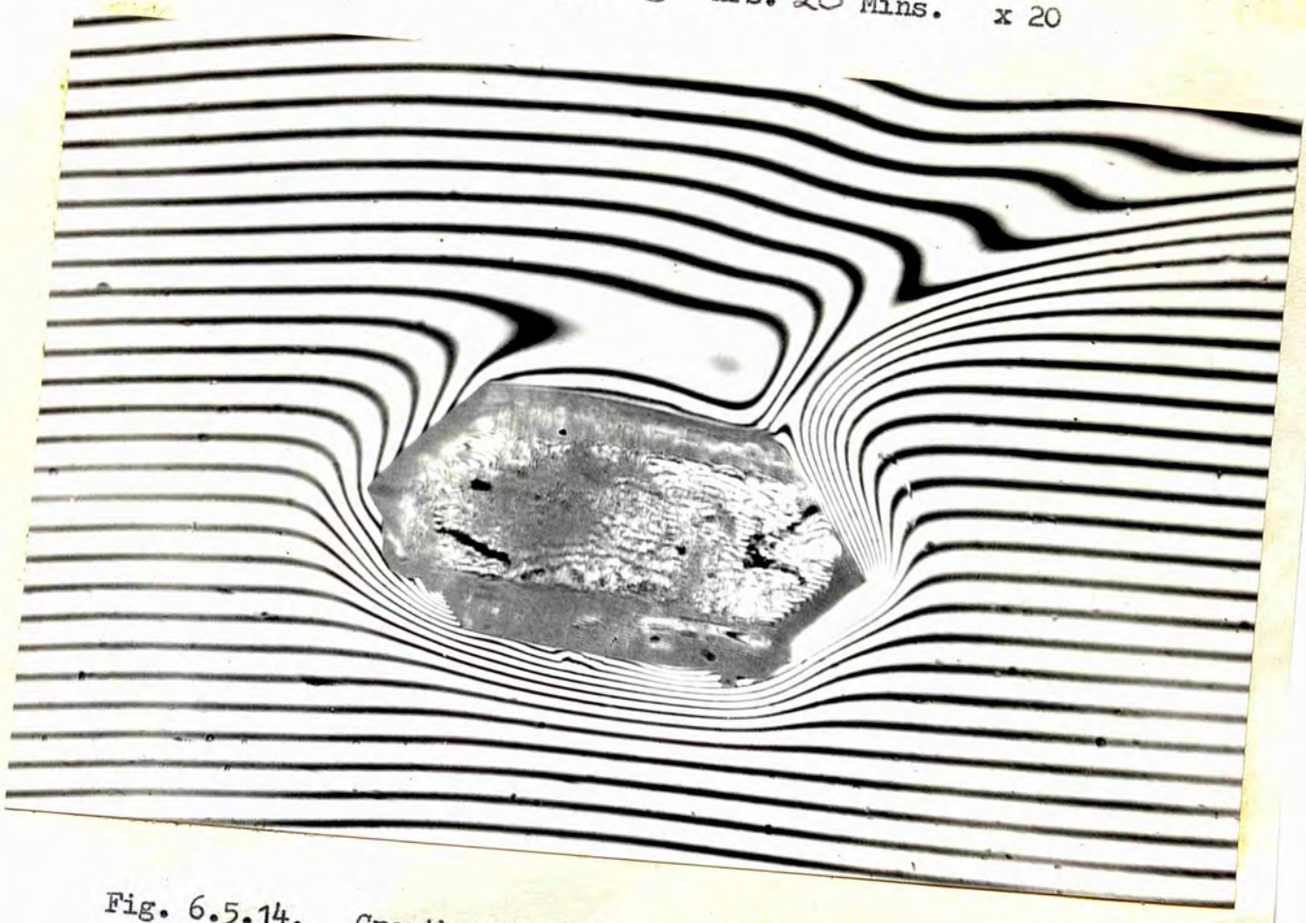


Fig. 6.5.14. Growth after 5 Hrs. 30 Mins. x 20

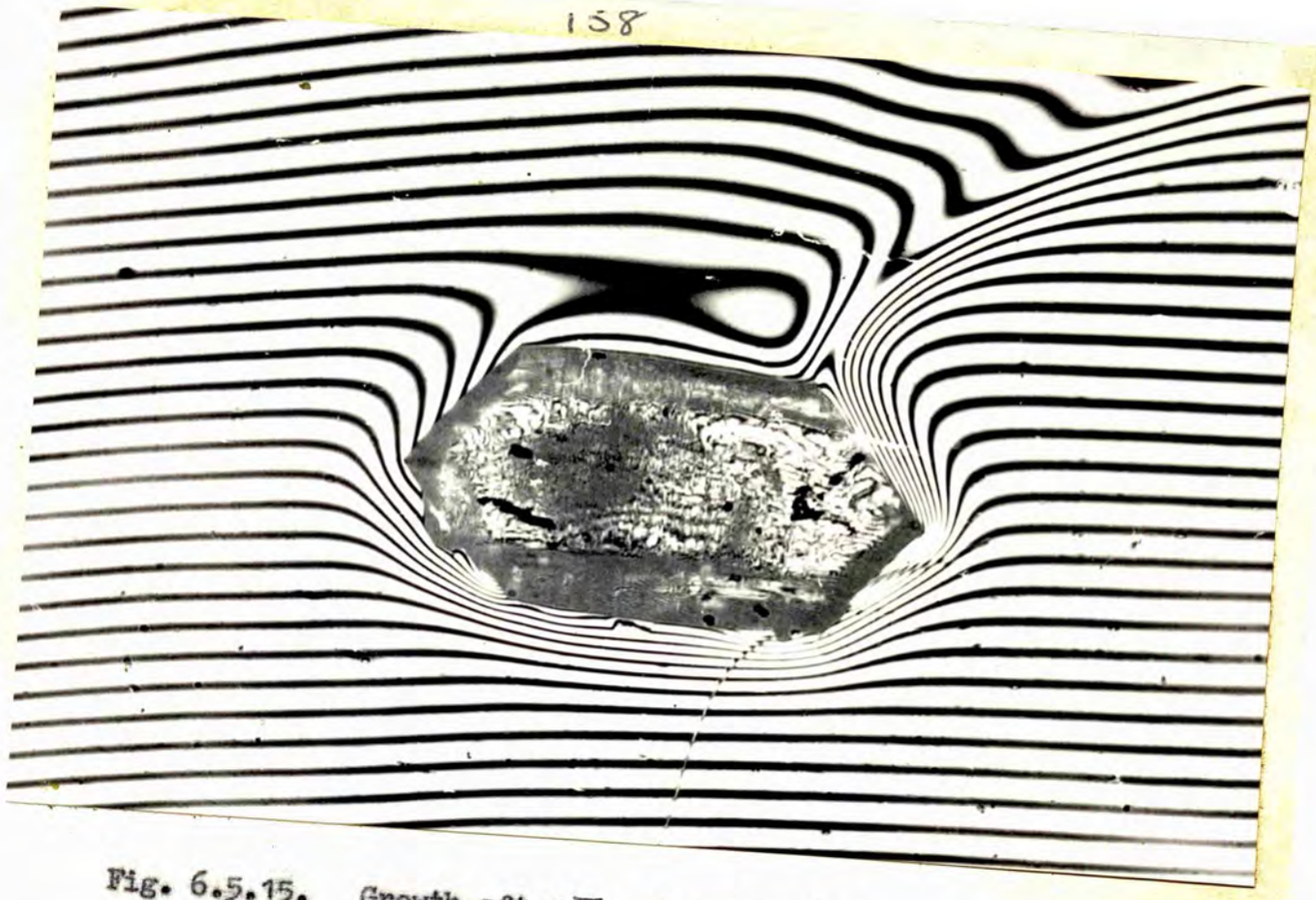


Fig. 6.5.15. Growth after 7 Hrs. 0 Mins. x 20

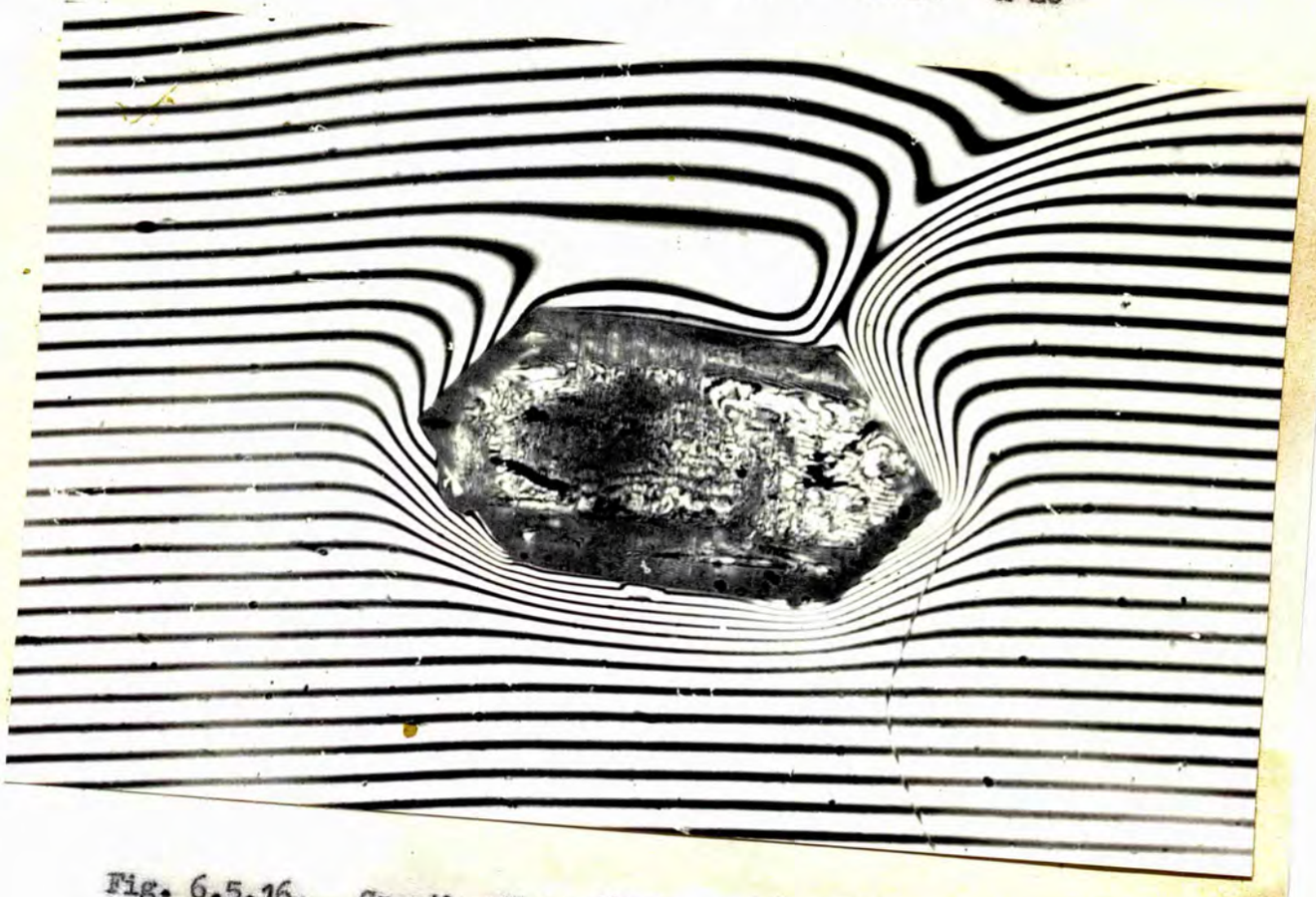


Fig. 6.5.16. Growth after 8 Hrs. 0 Mins. x 20

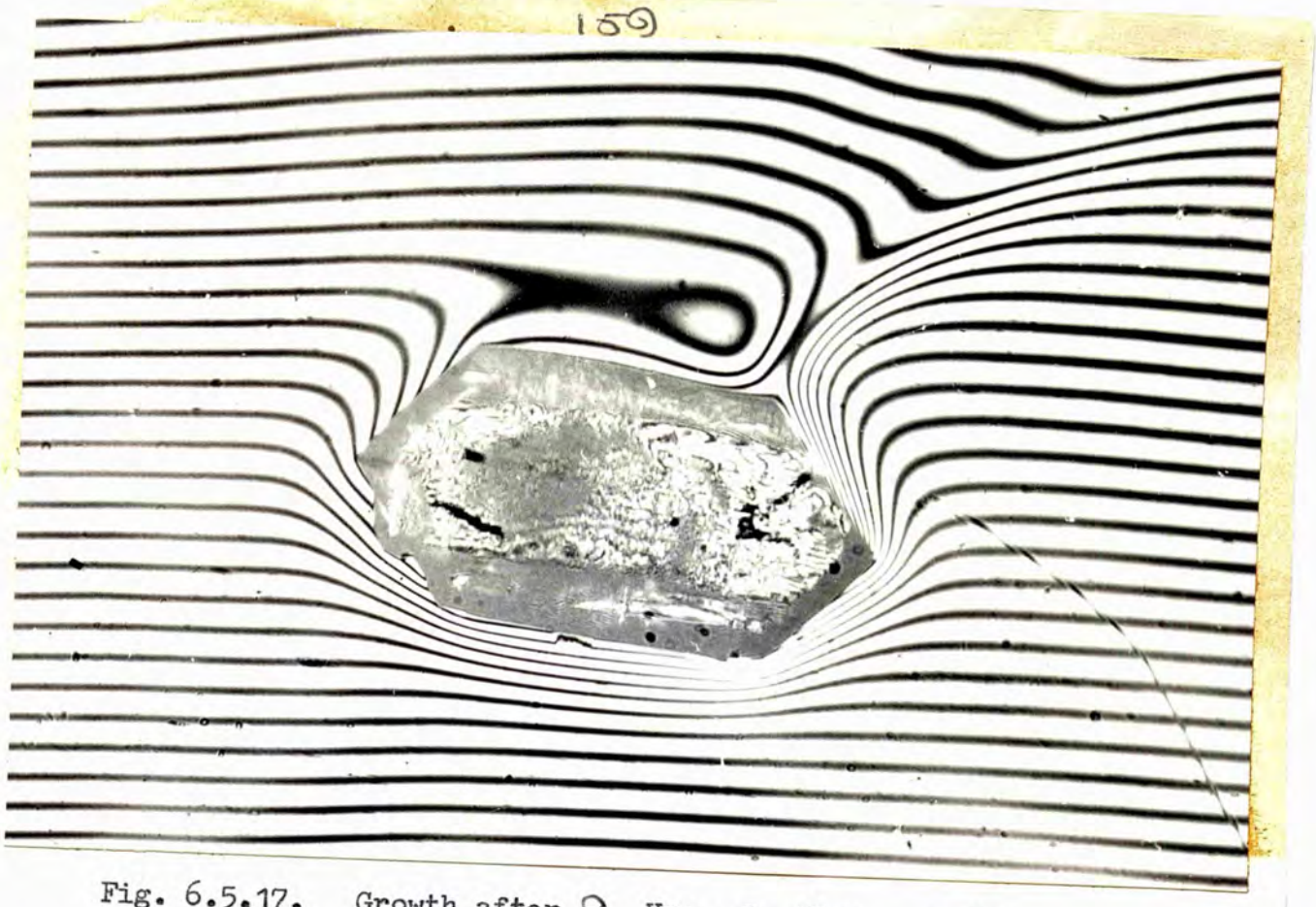


Fig. 6.5.17. Growth after 9 Hrs. 0 Mins. x 20

Fig. 6.5.18. Growth after 10 Hrs. 2 Mins. x 20

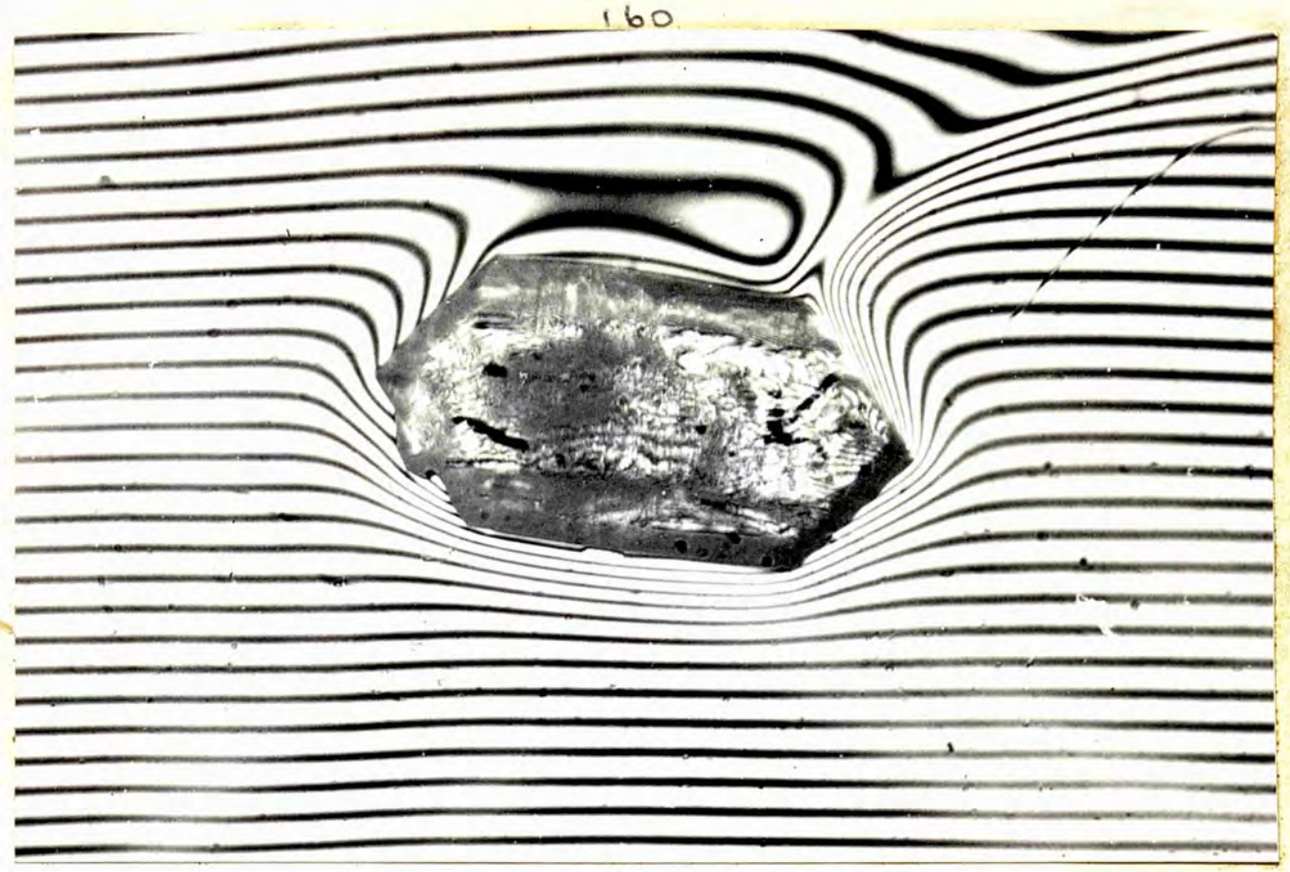


Fig. 6.5.19. Growth after 10 Hrs. 2 Mins. x 20

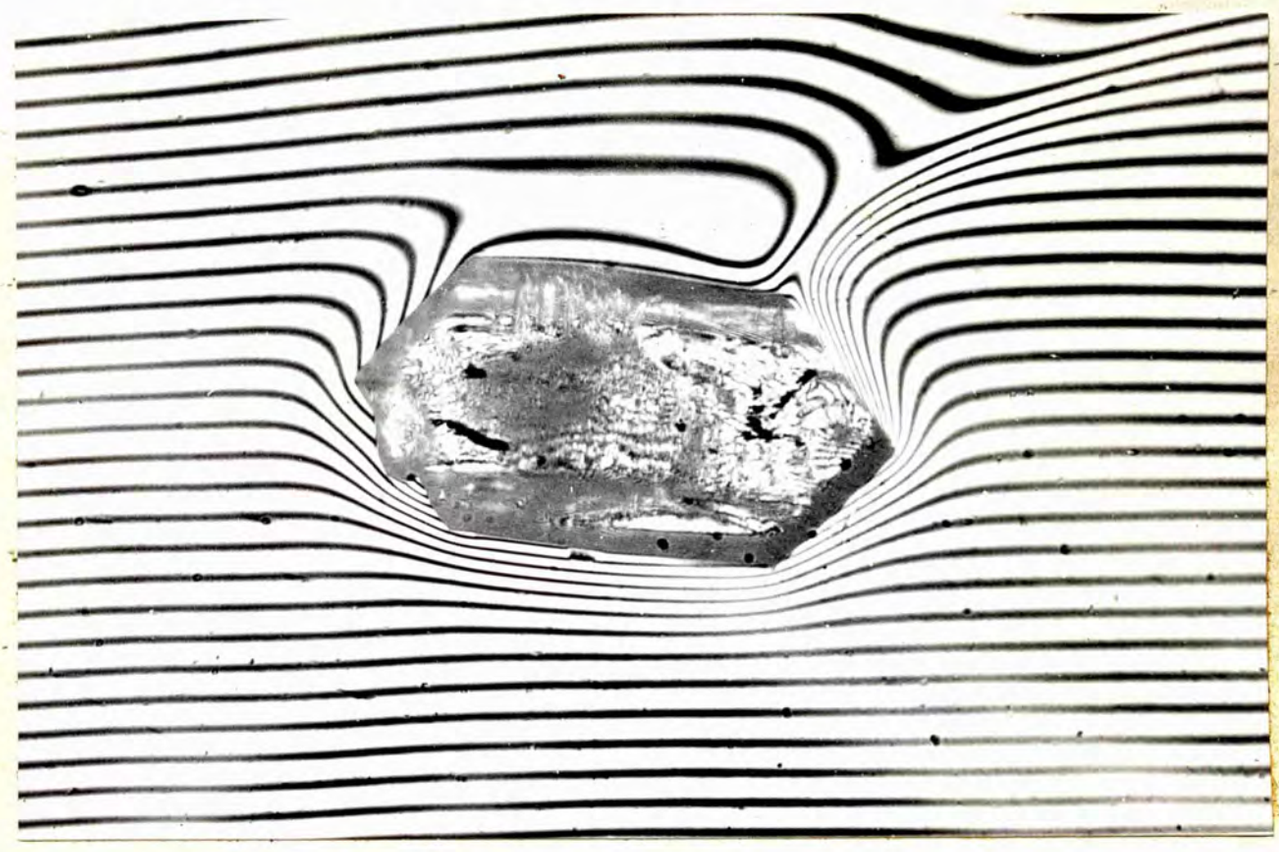


Fig. 6.5.20. Growth after 12 Hrs. 0 Mins. x 20

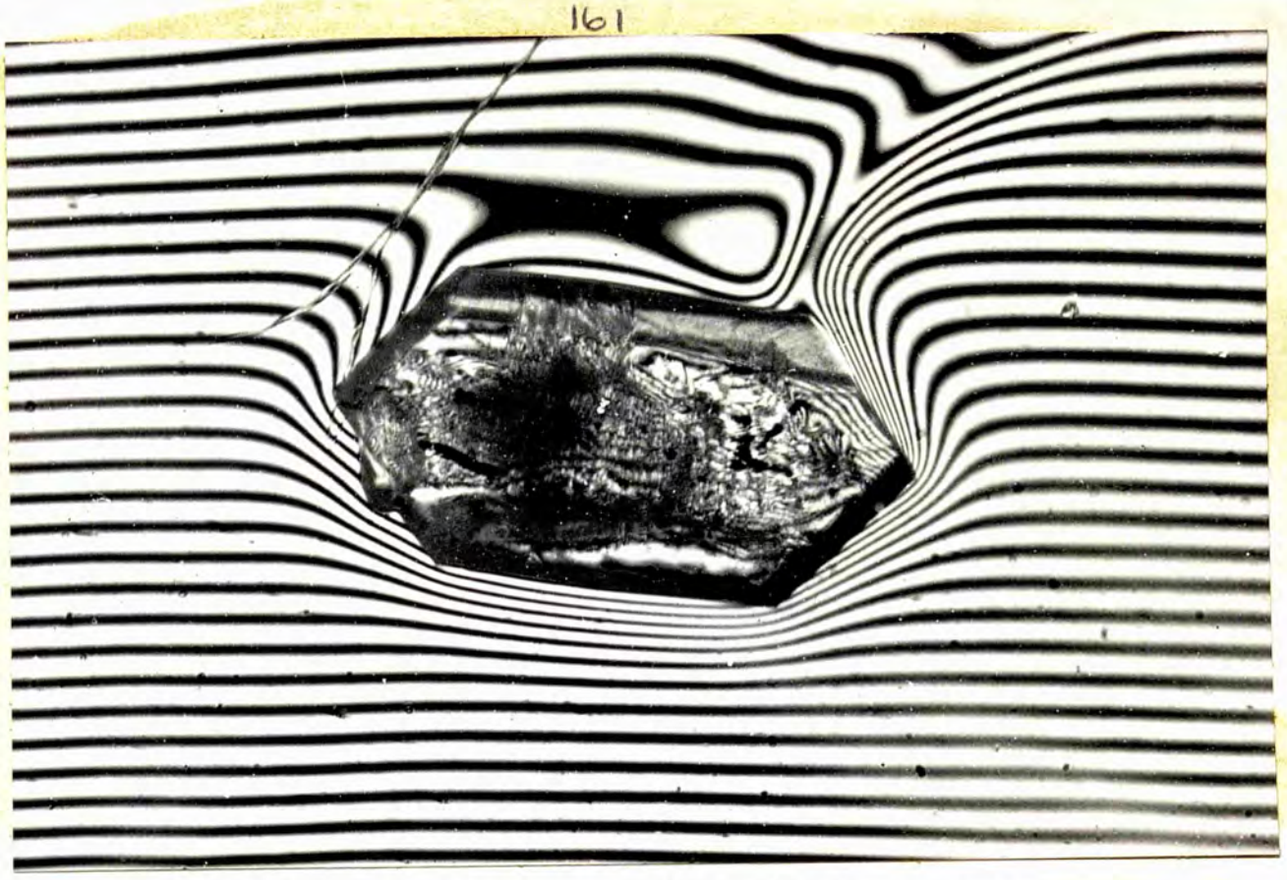


Fig. 6.5.21. Growth after 22 Hrs. 40 Mins. x 20

Fig. 6.5.22. Growth after 26 Hrs. 30 Mins. x 20

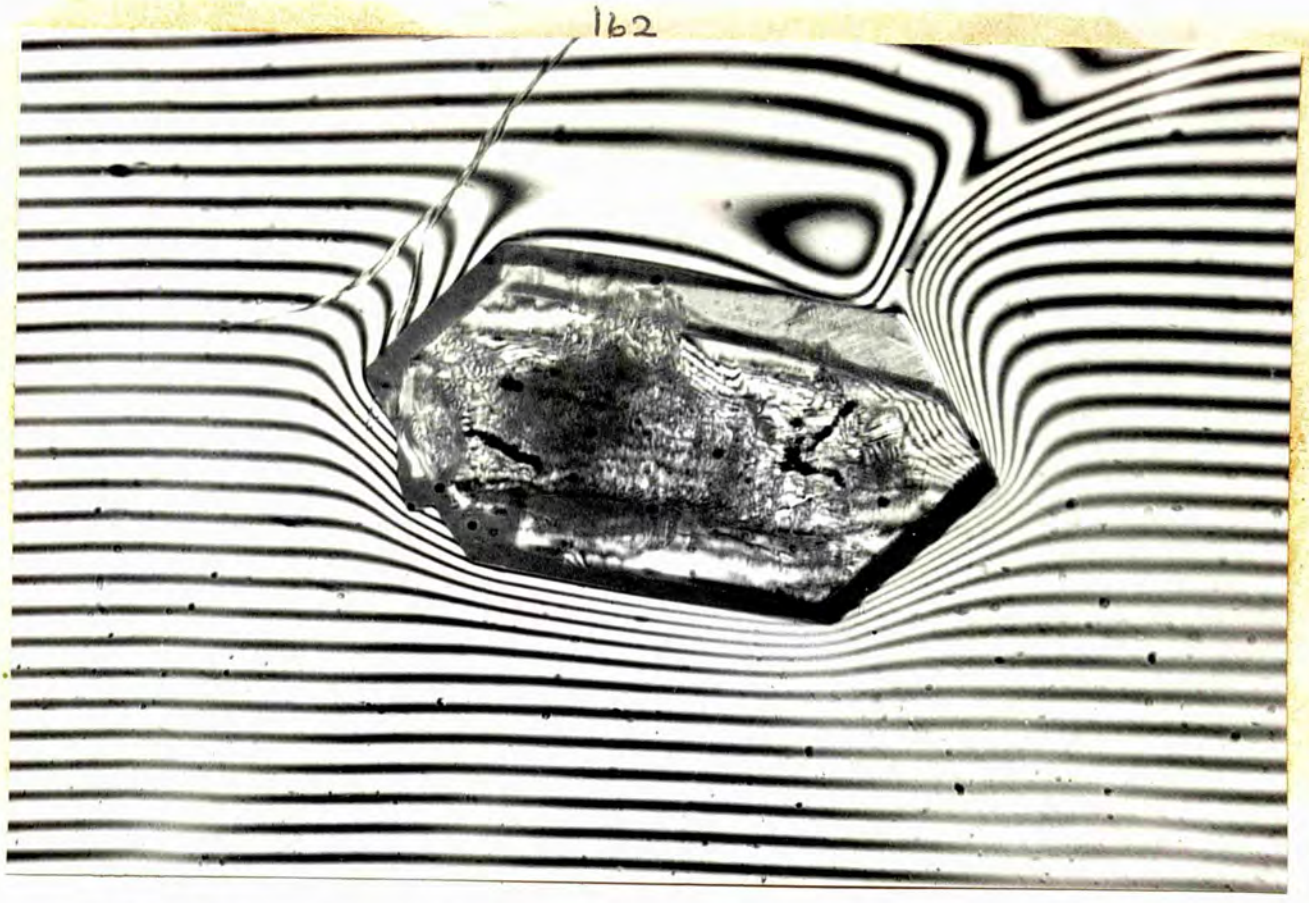


Fig. 6.5.23. Growth after 31 Hrs. Mins. x 20

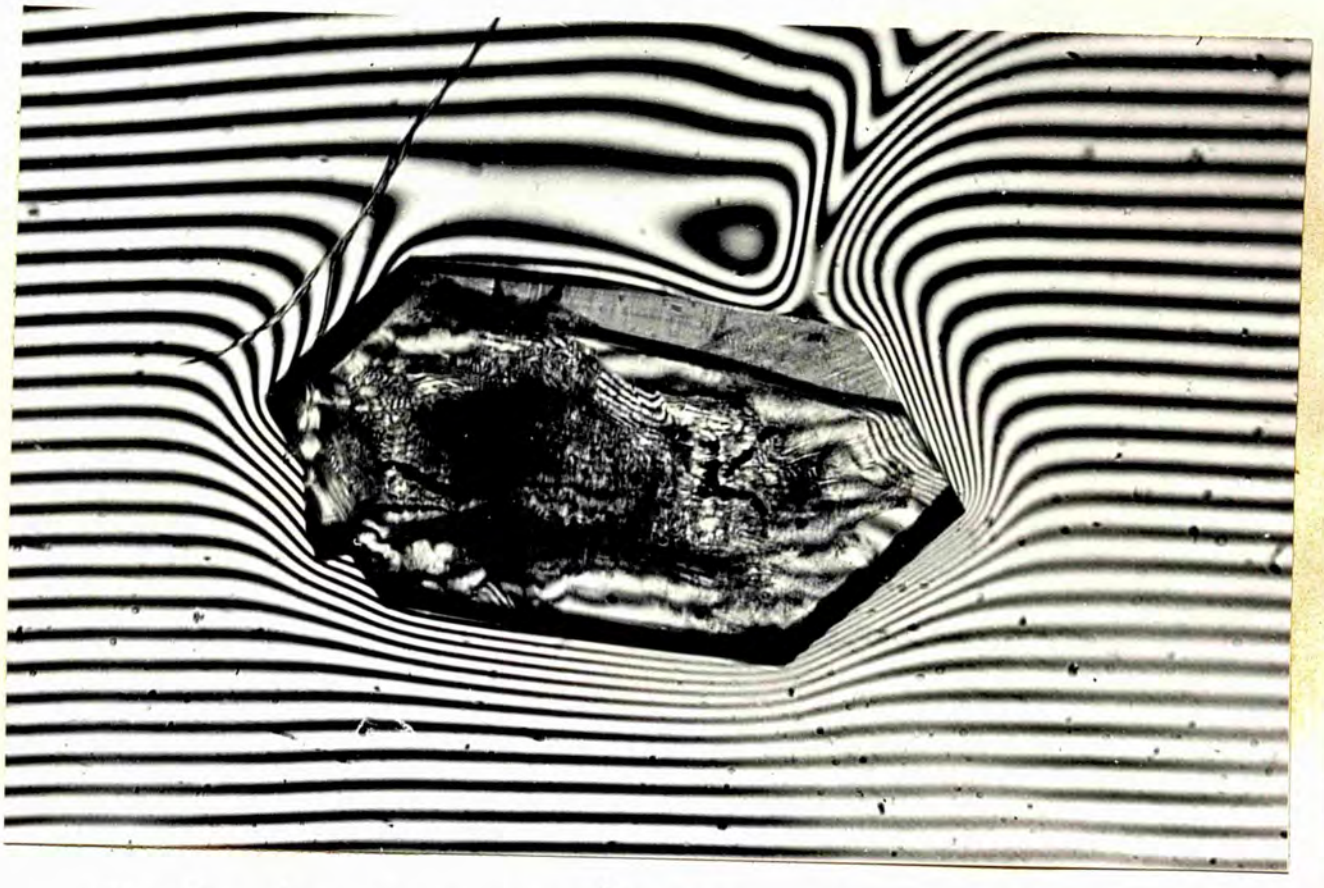


Fig. 6.5.24. Growth after 46 Hrs. Mins. x 20

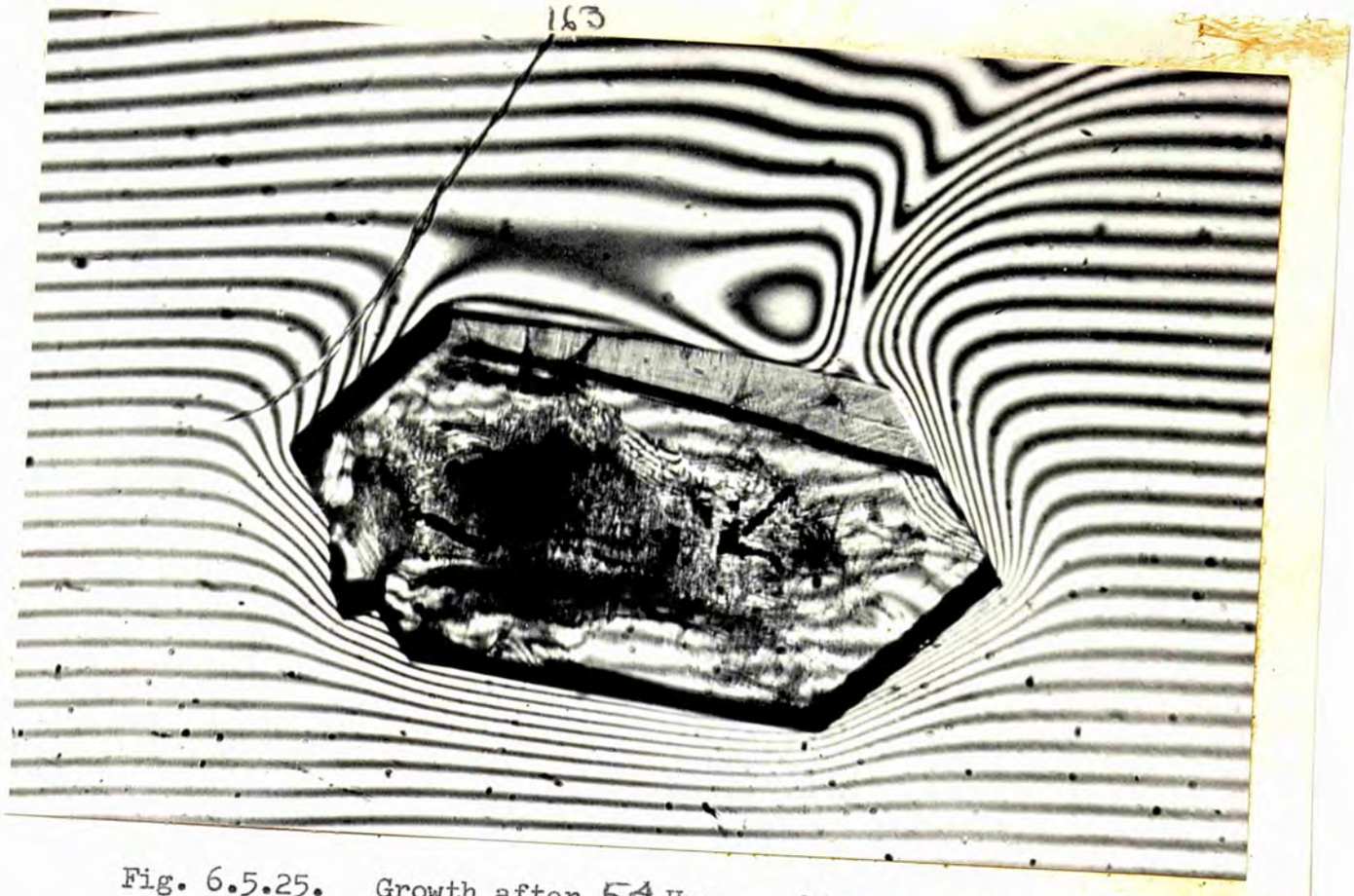


Fig. 6.5.25. Growth after 54 Hrs. Mins. x 20

Crystal 5.

This crystal was grown in a solution of 70.4% concentration.

The initial dissolution of the crystal extended over a period of about 14 mins. and is illustrated in Figs. 6.5.1 - 6.5.4. The crystal was unfortunately broken during the first moments.

Once again there is the marked effect of the corners C and F growing quite rapidly and becoming sharp. By chance there is a marking on this crystal in the form of an arrow and it can be seen from this that the face BC has not grown at all. It does appear as if that point, corner C, alone has grown and this quite rapidly during the eight minutes between Figs. 6.5.4 and 6.5.5.

As for the streaming, the beginnings of a lobe can be seen developing along face CD at a time of 46 mins. This is observed to move round the corner C and along the face BC where it breaks away into the solution. There is a slight indication of some movement at the corner F in Fig. 6.5.9. but this has disappeared 13 mins. later. The pattern of events then follows the normal course. Once the streaming had become established it remains at corner B throughout the period of growth.

The values of the changes in fringe order at each face of the crystal are shown in Fig. 6.5.26. and from table 6.5. the concentration may be calculated.

The crystal has completely 'healed' after about 7 hours.

(This never happened in the case of crystal 2, which was broken, and grew in a more concentrated solution). The value of the concentration along CD fluctuated until the face healed but then remained approximately constant for the remainder of the period of growth. At this face in Fig. 6.5.14 is a very steep gradient and the fringes are not resolved. The value of the concentration at this face must be only about 69% and yet during the next hour the defect in this face has disappeared completely. The concentration along the faces BC, EF and FA remains approximately constant throughout the whole period of growth. There was a decrease while the broken corner E healed. The concentration along the lower face followed the same pattern.

In the final picture can be seen the result of the growth of the crystal over a period of 54 hours. This again shows how the crystal has developed more on one side than the other and this would appear to be correlated with the gradient adjacent to the face, which throughout has been steeper at these faces which have been extended the most.

This concludes the chapter on the growth of ground crystals.

TABLE 6.5.1.

t = 0.175 cms.
μ_0 = 1.4660

Change in fringe order Δn	Change in refractive index $\Delta\mu$	Refractive index at face μ	Concentration at face C
3	0.0009	1.4651	70.0 %
4	0.0012	1.4648	69.85 %
5	0.0016	1.4644	69.7 %
6	0.0019	1.4641	69.55 %
7	0.0022	1.4638	69.45 %
8	0.0025	1.4635	69.3 %
9	0.0028	1.4632	69.2 %
10	0.0031	1.4629	69.05 %
11	0.0034	1.4626	68.95 %

FIG 6.5.2.6

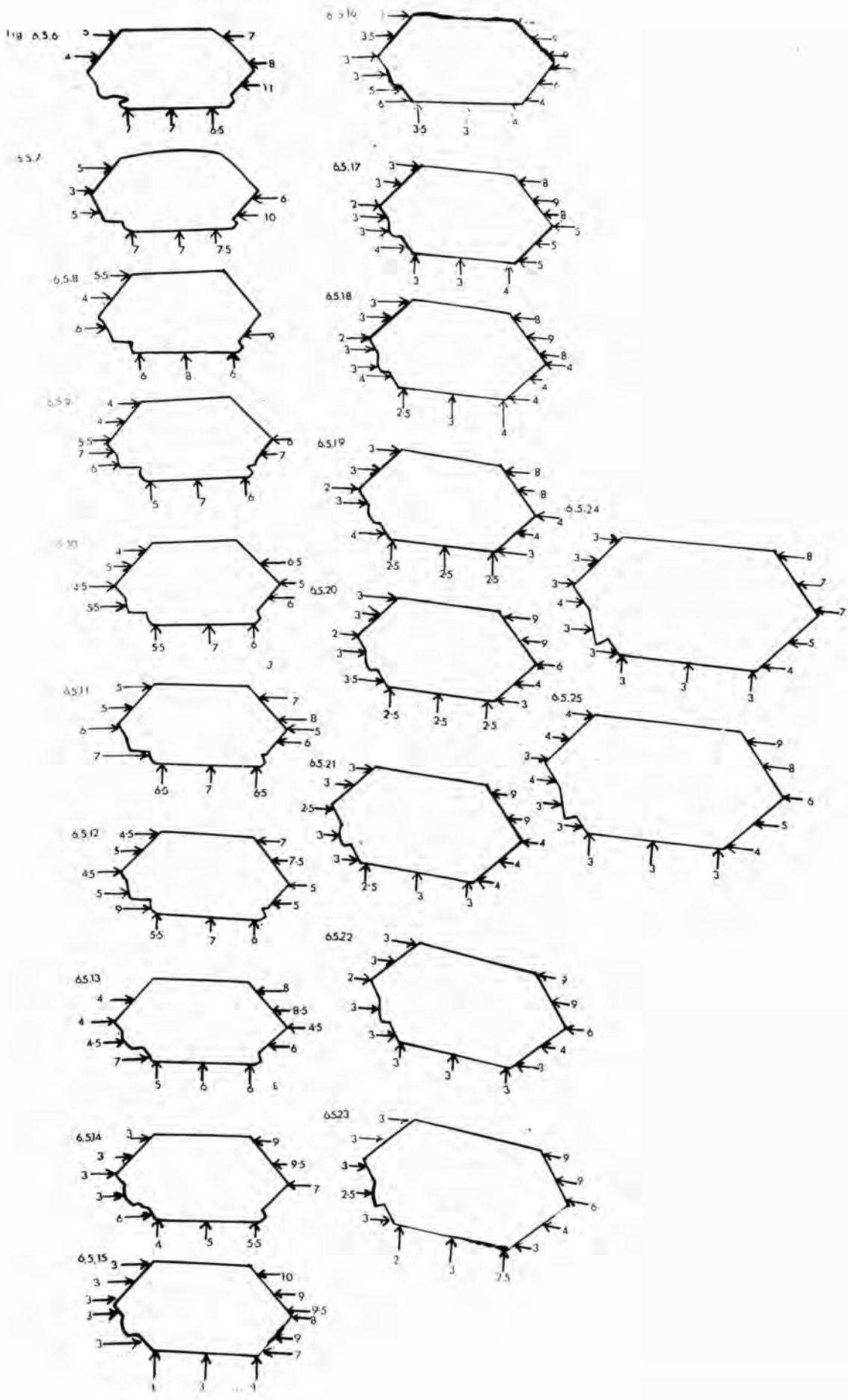


Fig 6.5.6
6.5.7
6.5.8
6.5.9
6.5.10
6.5.11
6.5.12
6.5.13
6.5.14
6.5.15
6.5.16
6.5.17
6.5.18
6.5.19
6.5.20
6.5.21
6.5.22
6.5.23
6.5.24
6.5.25

CHAPTER VII.

DISCUSSION OF RESULTS.

This work has been a preliminary study on the investigation of the effects of convection on the growth of crystals from solution. From the results it would appear that convection can play a major role in the process. Undoubtedly diffusion must occur but there are no indications of any extensive diffusion field. This is concluded from the fact that the fringes remained everywhere remarkably straight and parallel except close to the crystal where the effects of convection can be seen. This is observed in many of the photographs.

The most important effect to be observed from the photographs is the upward streaming in the solution as the crystal grows. This could be seen with such techniques as the Schlieren method which are purely qualitative. With the present interference method however the effect is very well illustrated and qualitative measurements of the concentration of the solution in the centre of this stream can be made and is found to have only decreased by approxi-1% relative to that of the bulk of the solution.

The rate at which the streaming is established would appear to depend on the concentration of the solution. For high concentration streaming occurred immediately and as the concentration

decreased there was an increasing time lag before streaming became evident. Once established the stream remained in existence for the remaining period of growth for which observations were made, and even in one case after 2 days was still in evidence. The stream also exhibited the property of movement along the upper face, no cause of this could be determined. However it always became finally established at the corner of the crystal.

From the results on the increase in area of the crystal with time and hence the measurement of growth rate, there would appear to be some correlation between growth rate and streaming. The observations on the rate of growth of the crystal indicated that it increased once streaming became established, and that fluctuations in the growth rate occurred when the streaming is undergoing variations. This however is not conclusive and it would be interesting to carry out an investigation on a simpler type of crystal e.g. cubic, in which the growth rate of the individual faces can be measured in order to test whether this apparent correlation is valid.

The concentration at the faces of the crystal has been measured. For the majority of crystals there was a concentration maximum at the corners but this was not always so. In certain cases the concentration along a face was constant over a long period of time. The value of the concentration at the face was certainly

never as low as the solubility concentration.

With reference to the adsorbed layer hypothesis no information has been gained. In this investigation the accuracy of the method did not justify any calculation of the concentration gradients and these have only been estimated qualitatively. Sometimes even this was not possible, for crystals grown in the more concentrated solutions. Under these circumstances very steep gradients occurred and the fringes were most difficult and sometimes impossible to resolve. Some refinements in the experiment would be required. A more accurate determination of the initial refractive index of the solution is necessary. It would also seem desirable that the solution should be caused to nucleate and produce its own seed crystal rather than continuing the growth of a previously grown crystal . This would be advantageous from a number of points of view. In the present work, as the cell in which growth took place was very thin and the viscosity of sucrose solutions relatively high, the initial stages of the experiments had to be performed with warm solution thus causing dissolution of the crystal in the first stages and a corresponding change in the initial concentration of the solution.

It would be interesting as stated above to carry out the measurements of concentration gradients on a simple cubic crystal, this would make computation easier and would test whether under

the conditions of an experiment such as this whether in fact there is a greater flux of solute in the centre of the crystal face thus creating the necessity for postulating an adsorbed layer which was required by the results of Bunn, Berg and Humphreys-Owen.

It would also seem necessary that in order to standardize the experiment a constant temperature enclosure should be constructed. These experiments were all carried out a room temperature which was approximately 20° C., but this could vary as much as 5° C.

It appears likely from these experiments that there is some form of layer flow round the crystal as the stream usually breaks away from the crystal at one point. For this to occur the depleted solution would have to flow round the various faces of the crystal.

Another point of interest which could be followed up is the investigation of the reaction between the convection streams due to two crystals placed near one another in solution in order to study any interaction in the field around growing crystals. This experiment can also be adapted to study growth with the cell in a horizontal position, and with a cell of suitable thickness e.g. 1 to 2 z 10^{-3} cm., so that convection could be considered as eliminated, the effect of diffusion on growth could be studied.

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